UNITED STATES ATOMIC ENERGY COMMISSION

34262

CHEMICAL PROPERTIES OF URANIUM HYDRIDE

by

James Curren Warf

Iowa State College

September 29, 1949

This copy is reproduced direct
from copy as submitted to this office

Technical Information Branch, Oak Ridge, Tennessee
AEC, Oak Ridge, Tenn., 10/14/49--95-A11185

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DECLASSIFIED

TABLE OF CONTENTS

SECRET

3-l-295

CHEMICAL PROPERTIES OF URANIUM HYDRIDE

ABSTRACT

There are only two references to uranium hydride in the chemical literature prior to the existence of the Manhattan Project. The first of these gave no valuable information; the second was a patent issued in 1931 of a general method of preparing metal hydrides. The reaction of hydrogen with the electrolytic uranium available at that time was found to take place above 200°, and a crude dissociation pressure-temperature curve was given. No chemical or other physical properties were presented.

The intensive investigations of uranium hydride on the Manhattan Project began early in 1943, when it was found that massive uranium metal of high purity, available for the first time, reacted with hydrogen at 250° forming a black, pyrophoric powder. By thermal decomposition of the hydride finely divided and exceedingly reactive uranium was produced. This powdered metal reacted rapidly with hydrogen even at room temperature, with considerable heat being generated. Uranium hydride was also found to be produced by the action of steam on uranium at 250°, and by

the action of tetralin or decalin on uranium, reactions which also yielded naphthalene. Deuterium was observed to react with uranium at 250°, forming uranium deuteride.

Analysis of uranium hydride by combustion and weighing the water formed, by weight gain on formation, and by weight loss on decomposition, showed that there were 2.97 hydrogen atoms for every uranium atom. It was demonstrated that the ratio of hydrogen to uranium atoms in the hydride, counting only the uranium not combined with the impurities originally present in the metal (carbon, iron, oxygen, etc.), was 3.00, making the formula of uranium hydride UH_3.

The physical and thermodynamic properties of uranium hydride were summarized. Formed at atmospheric pressure, the hydride particles easily passed through a 400 mesh sieve, but formed at high pressures, the product consisted of much larger fibrous crystals. X-ray diffraction analysis disclosed the crystal structure of UH_3 as cubic, totally unrelated to the structure of the metal, which is orthorhombic. The unit cell of the hydride, containing eight molecules, was found to be 6.631 A on edge, corresponding to an x-ray density of 10.92 $\pm$ 0.01 g./cc. The respective figures for uranium deuteride were 6.620 A and 11.11 $\pm$ 0.01 g./cc. The particle densities of uranium hydride and deuteride, measured by the use of a helium densitometer, were 10.95 $\pm$ 0.1 and 11.20 $\pm$ 0.1 g./cc., while the bulk density was about 3.4 g./cc. A

series of measurements of the densities of U-UH$_3$ and U-UD$_3$
mixtures, as a function of the composition, showed that the
relationship was linear within the limits of experimental error.
This established that the systems were either two-phase
systems (U and UH$_3$ phases or U and UD$_3$ phases) or perfect
solid solutions. X-ray analysis showed that the hydride
could not be a solid solution, and was in all probability
a true chemical compound.

Pressure-composition isotherms for uranium hydride had
a steep rise at the uranium side to a long horizontal section
representing a constant pressure. The curves corresponding
to formation of the hydride then rose rapidly on the uranium
side, but the curves corresponding to decomposition contained
a pronounced dip at about 98 mol per cent hydride, just after
the horizontal, constant pressure section. An explanation
for this unexpected dip is lacking. It was found that hydro-
gen did not transfer from the hydride to the powdered metal
in a system maintained at 325°. Dissociation pressure-temper-
ature studies showed that the Clausius-Clapeyron equation was
obeyed. The pressure for the deuteride was always about 1.4
times that of the hydride. The equations for the dissociation
pressures (in mm.) as a function of temperature were:

Hydride $\qquad \log p = \dfrac{-4500}{T} + 9.28$

Deuteride $\qquad \log p = \dfrac{-4500}{T} + 9.43$

Calculations based on the above data using the van't Hoff

reaction isochore showed that the heat of the reaction

$$U + 3/2\ H_2\ \longrightarrow\ UH_3$$

was $\Delta H = -30.8$ kg.-cal. Direct measurement gave $\Delta H = -30.5$

kg.-cal. Attempts to separate deuterium from hydrogen employ-

ing the hydride reaction were fruitless.

It was found impossible to preferentially leach the

fission products from uranium hydride prepared from metal

previously subjected to deuteron bombardment in the cyclotron.

Gaseous fission products did not escape on conversion to

hydride.

The chemical properties of the hydride were investigated

in some detail. Although pyrophoric, the hydride could be

rendered air-stable by gradual exposure to air, which caused

partial oxidation. Although nitrogen and carbon dioxide had

little effect at room temperature, the hydride, once ignited,

continued to burn in these gases. Added gradually, water caused

the evolution of some heat, but had little other effect;

addition in a large amount at a time caused deflagration.

The non-oxidizing acids when dilute very slowly dissolved

the hydride, but hot concentrated sulfuric acid was reduced.

Nitric acid, or acidified oxidizing agents such as hydrogen

peroxide, dissolved the hydride forming uranyl salts. Organic

solvents were without effect, except for the chlorinated

hydrocarbons, which were decomposed, sometimes with violence.

The more soluble silver salts reacted smoothly with uranium

hydride, liberating silver metal in a spongy form; the per-
chlorate ion of silver perchlorate was also reduced, yielding
silver chloride. Other heavy metal salts reacted with the
hydride as well.

It was observed that the various halogen-bearing gases
reacted with the hydride, generally at $250°$, yielding uranium
halides in fine, conveniently-handled powders. Thus hydrogen
fluoride gave uranium tetrafluoride, hydrogen chloride gave
uranium trichloride, and hydrogen bromide gave the tribromide;
the latter two halides were oxidized by chlorine and bromine
vapor to the respective tetrahalides. Steam reacted with the
hydride yielding uranium dioxide, hydrogen sulfide gave
uranium disulfide, ammonia gave a nitride, and phosphine gave
the sesqui-phosphide, U_2P_3. These reactions served admirably
as preparative methods. By the use of uranium hydride and
certain compounds readily prepared from it, thorough purifi-
cation of several common laboratory gases was achieved. Hydro-
gen chloride, for example, was freed of moisture, oxygen,
and chlorine by passing over heated uranium trichloride. The
rare gases could be rigorously purified by passing over
powdered uranium at $700°$; hydrogen or deuterium could be simi-
larly treated, or could be generated by thermal decomposition
of the hydride or deuteride.

Attempts were made to reduce organic compounds with
uranium hydride. Although reactions occurred, none of the
expected products could be isolated.

By mixing uranium hydride intimately with uranium tetrafluoride and heating to $1100°$, the hydride was decomposed, and the uranium liberated reduced the tetrafluoride to uranium trifluoride, previously unknown. The trifluoride was a dense black, coke-like solid. X-ray analysis showed that its crystal structure was hexagonal, with two UF_3 molecules per unit cell, with $a = 4.13$ A and $c = 7.33$ A. Heating above $1600°$ caused disproportionation into uranium and uranium tetrafluoride the latter of which sublimed away.

The evidence quite strongly suggested that uranium hydride is a salt-like hydride, in the same class as sodium and calcium hydrides, rather than an interstitial compound, as is the case with palladium hydride.

Uranium hydride formed what appeared to be solutions in mercury. These were termed "amalgams", although they were probably not true solutions, since mercury nearly free of uranium could be separated by centrifugal filtration, and since amalgamation of uranium hydride containing radio-xenon (from the disintegration of a fission product) did not cause the liberation of this gas. The amalgams varied in consistency from a fluid through a semi-solid to a gray powder with increasing hydride concentrations, and some of them had a remarkable tendency to adhere to glass, forming a mirror. The hydride was found to be precipitated from its amalgam by the action of air, water vapor, or hydrogen sulfide. The product so obtained had an H/U ratio con-

siderably lower than three, showing partial attack by the

air, water, or hydrogen sulfide. The amalgams were most

probably colloidal suspensions.

Uranium hydride and the hydride reaction proved to have

a number of practical applications. These included: labo-

ratory source and reservoir of pure hydrogen and deuterium,

preparation of powdered uranium, preparation of uranium

compounds, isolation of intermetallic compounds of uranium,

etching of metallographic specimens, ▨▨▨▨▨▨▨▨▨▨

▨▨▨▨▨▨, maintaining a given hydrogen or deuterium

pressure, and analysis of metallic uranium for the free

element.

I. INTRODUCTION

A general investigation of the chemical properties of uranium and related materials was underway in the various laboratories in the United States in 1942, first under the auspices of the National Defense Research Council (NDRC), and later under the Manhattan District or Manhattan Project of the War Department. The Project at Iowa State College, under the direction of Dr. F. H. Spedding, had two principal divisions: a section devoted primarily to the development of methods for the manufacture of pure uranium metal on a large scale, and a section to carry out researches into the chemical, radiochemical, and physical properties of uranium, the trans-uranic elements, thorium, the fission products, and other materials. A process was developed (1) and large amounts of pure uranium were manufactured by the first section, and were available for research purposes.

Methods of analysis of uranium for many trace impurities were being developed by a group under the direction of the writer, and in addition investigations into the general chemistry of uranium were undertaken. In March, 1943, an analytical scheme for the determination of traces of calcium in uranium was being developed, during which the first pure sample of uranium hydride was prepared, the purpose being to leach the calcium from the finely divided hydride. Although this

original aim was unsuccessful, uranium hydride itself proved
to be such an interesting substance that the primary attention
was directed to it. In the course of the next three years the
chemical and physical properties of uranium hydride were the
subject of extensive researches by a number of different in-
vestigators; the present writer's efforts were concentrated on
the chemical aspects more than the physical.

The reasons for the investigation, aside from the general
scientific interest by Project chemists in uranium hydride, were:
(a) the possibility of leaching fission products from uranium
hydride prepared from metal from the piles, (b) the possible
analogy of uranium hydride to plutonium hydride, which had not
been prepared at that date, (c) the corrosion of uranium by
hydride formation in water-cooled piles, (d) the possible use
of uranium deuteride in the place of frozen heavy water as a
target for deuteron bombardments in investigating the reaction

$$d + d \longrightarrow He^3 + n$$

and (e) the possible use of hydrides or deuterides as moderators
for neutrons. Quite a number of additional applications and
uses of uranium hydride have been discovered or developed, and
are discussed subsequently.

Part V (Resumé of Physical Properties of Uranium Hydride
and Deuteride) is abbreviated and is included for completeness
and to make the following parts more readily understandable,
although the present writer did only a minor part of the actual
experimental work described in this section. Credit is given

to the investigators upon whose work these parts are based in
footnotes in the appropriate places, in the literature cited,
and again in the Acknowledgements. This also applies to four
subsections in Part VI and to one subsection in Part VII.

II. LITERATURE SURVEY

While conducting some experiments in 1912 on the solu-
bility of helium and argon in a number of metals at elevated
temperatures, Sieverts and Bergner (2) treated some crude
uranium powder with these gases and also with hydrogen. They
noted that at 1100° a 100 g. sample of the impure metal ab-
sorbed 1.6 mg. of hydrogen when the pressure was 760 mm. The
uranium they had available undoubtedly contained a large
fraction of uranium dioxide.

The only other mention in the pre-Project literature is
in a patent granted to Driggs (3) in 1931, which describes a
general method of preparing metal hydrides. According to
this source uranium hydride was formed when the metal, a
sintered powder prepared electrolytically and containing con-
siderable oxide, was heated to $200-225^{\circ}$ in hydrogen. A temper-
ature-dissociation pressure curve was given which has proved
to be in modest agreement with the recent data; for example
Driggs gave the dissociation pressure of hydrogen at 300° as
about 20 mm., while the most recent determination (see Part V)

is 27.6 mm. Driggs recognized that the reaction of uranium
with hydrogen was exothermic, and gave the formula of the
product as UH_4; it is now known to be UH_3. No chemical or
other physical properties were presented.

The earliest experiment (June, 1942) by Project investi-
gators involving uranium hydride was an incidental preparation
of the material during an attempt to cast uranium in a hydrogen
atmosphere (4). The formation of a dark, pyrophoric powder
was recorded, but the work was not further pursued. It was
March, 1943, when the extensive researches noted earlier were
initiated, after the present writer (5, 6) converted a sample
of pure, massive uranium to the hydride by heating it to 250°
in a current of hydrogen.

III. PREPARATION AND COMPOSITION OF URANIUM HYDRIDE

A. Formation, Appearance, and Recommended
Procedure for Preparation

In the first experiment designed to prepare uranium
hydride, with the aim of leaching out the calcium impurity
for analytical purposes as explained earlier, two grams of
oil-free uranium turnings in a porcelain boat was heated by
a resistance furnace in a stream of hydrogen. The exhaust
hydrogen was bubbled through water while the furnace temper-
ature was slowly raised. When the temperature was about

250°, the rate with which the exhaust hydrogen bubbled through the water markedly decreased for a few minutes, and then rose to its original rate. This showed that a certain amount of hydrogen had been absorbed. After cooling to room temperature the boat was withdrawn, and was filled with a dark gray powder.

The hydrogen for the above experiment was prepared by the action of sulfuric acid on zinc, and was dried with calcium chloride. In the next experiment commercial tank hydrogen was employed, and it was found that the reaction did not occur until the temperature had been 250° for some time. An investigation of the cause of this delayed reaction (7.) disclosed that it was due to the presence of oxygen in the hydrogen (the tank gas contained 0.5 per cent oxygen). When the oxygen impurity was removed, no delay in the initiation of the reaction was encountered. A widely used method of removing the oxygen from hydrogen is to pass the gas through a tube packed with copper turnings heated to a red heat; this converts the oxygen to water, which is removed by a dehydrating agent such as magnesium perchlorate. While this technique was satisfactory, it was found that even more rigorous purification of the hydrogen could be effected by passing it through uranium turnings or powdered uranium heated to 700° (see p.55). While oxygen impurity in the hydrogen caused a delay in the reaction when uranium hydride is formed, it was found that an oxide layer on the uranium used had little effect, and required removal only if it constituted an undesired impurity in the hydride prepared.

As ordinarily prepared uranium hydride was an exceedingly

fine powder with a black or very dark gray color. Close ex-

amination showed a few small, shining particles (inclusions)

scattered throughout the powder; these were probably the im-

purities of the metal, principally uranium carbide, nitride,

oxide, etc. The preparations were generally very pyrophoric.

Based on the experience with the above and numerous ad-

ditional experiments, the following general procedure for the

preparation of uranium hydride is presented.

Recommended Procedure for the Preparation of Uranium

Hydride. The hydrogen used is purified whether it is

generated in the laboratory or is commercial tank hydrogen.

The apparatus is shown in Fig. 1. Sufficient purification

is achieved for most work by leading the gas through a

quartz, Vycor, or Pyrex #172 tube packed with fine copper

turnings and heated to 650-700° in a resistance furnace,

and then through a second tube containing anhydrous mag-

nesium perchlorate. The most exact work required more

rigorously purified hydrogen, which is accomplished by

passing the hydrogen from the above treatment through a

vertical tube (quartz, Vycor or Pyrex #172) containing

uranium powdered by conversion to the hydride followed

by thermal decomposition. This tube is maintained at

700-750°. Fine glass wool filters are inserted at either

end to prevent any of the fine solid particles from being

carried mechanically into other parts of the apparatus.
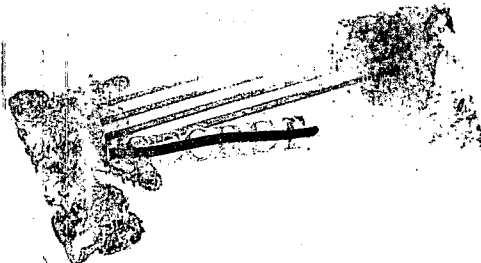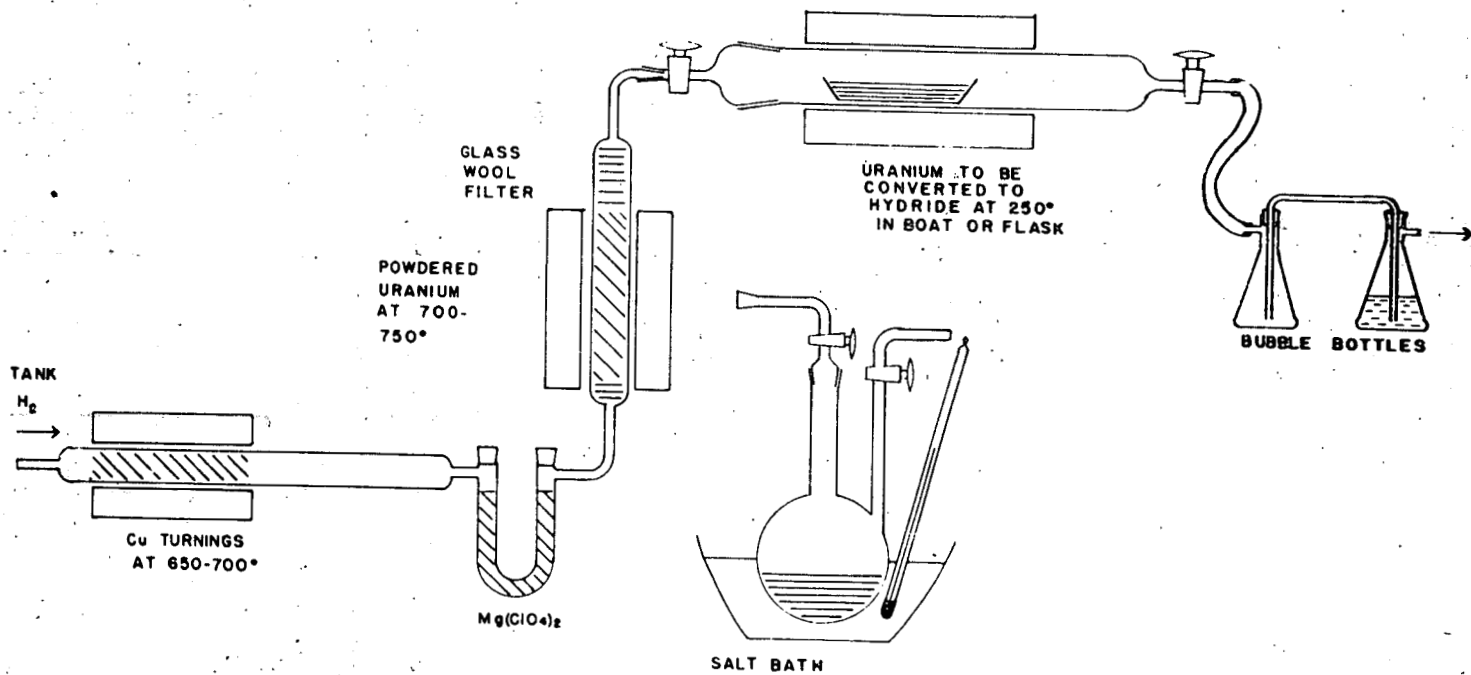
GLASS
WOOL
FILTER

URANIUM TO BE
CONVERTED TO
HYDRIDE AT 250°
IN BOAT OR FLASK

POWDERED
URANIUM
AT 700-
750°

TANK
H$_2$

Cu TURNINGS
AT 650-700°

Mg(ClO$_4$)$_2$

SALT BATH

BUBBLE BOTTLES

ISC-50

21

FIG.1 APPARATUS FOR PREPARATION OF URANIUM HYDRIDE

The uranium to be converted to the hydride, in the form of turnings or a massive lump, is cleansed of any oil with carbon tetrachloride or other solvent, dried, and is treated with warm dilute nitric acid until the oxide is completely removed. The shiny metal is washed thoroughly with water and distilled water, followed by alcohol and ether. After drying the metal is inserted into the reaction tube or flask, which is provided with a suitable heating means and thermometer. Horizontal tubes are best heated with a hinged-top resistance furnace, while flasks are conveniently heated with the aid of a low-melting nitrate-nitrite salt bath (8). The reaction vessel must be large enough to accommodate at least a ten-fold expansion as the metal is converted to the hydride. Rubber connections are satisfactory for preparations at atmospheric pressure, but ground glass joints are best for reduced pressure. The exhaust hydrogen is conducted through a trap to a bubble bottle, where its rate may be checked, while a vacuum apparatus is equipped with a manometer, the exhaust hydrogen escaping through a stopcock to the pump.

The air in the reaction vessel is flushed out with the purified hydrogen at room temperature, and then the temperature is gradually raised. The metal keeps its luster up to about 200–210°, when it becomes coated with a thin layer of the hydride, which gives the surface a bluish appearance. This color changes as the temperature

is raised, becoming iridescent, and finally dark. At
245-250°, the hydride flakes off as a black powder,
exposing fresh surface. When massive lumps of uranium
are used, the reaction vessel should be tapped periodi-
cally to aid in shaking the hydride loose. The reaction
is complete when, on shutting off the hydrogen supply,
the water in the bubble bottle is not drawn back, or in
the case of a vacuum apparatus, the manometer shows no
change in pressure when the hydrogen supply and exhaust
stopcocks are closed. One hundred grams of uranium
turnings are completely converted to the hydride in 25
to 30 minutes, while a lump of the same mass requires
90 to 120 minutes.

B. Formation of Uranium Hydride from the Powdered Metal

The powdered uranium prepared by the low-temperature decom-
position of the hydride (pp. 16 and 85) proved to be exceedingly
reactive. Specimens sometimes caught fire in a carbon dioxide-
filled dry box. They absorbed hydrogen rapidly even at room
temperature, and became hot. Experiments showed that at the
temperature of solid carbon dioxide (-76°) hydrogen was slowly
absorbed (9).

C. Formation of Uranium Hydride Under an Inert Solvent

In connection with the attempts to hydrogenate organic compounds under the influence of uranium (p. 57), it was desired to determine the effect of an inert solvent on the formation of uranium hydride. A few grams of clean uranium turnings were covered with mineral oil in a flask holding a delivery tube reaching to its bottom, and hydrogen was bubbled in while the apparatus was being heated to 250° (7). The uranium was only very slowly attacked, and a black deposit collected in the lowest part of the flask. The rate of reaction was perhaps one hundredth of the rate in the absence of the mineral oil. The slowness of the reaction was believed attributable to two factors: the low solubility of hydrogen in the solvent at 250°, and the manner in which the mineral oil caused the hydride layer to adhere to the metal, forming a protective coating.

D. Formation of Uranium Hydride by the
Action of Steam on Uranium

As pointed out in the Smyth report (10) the corrosion of uranium slugs by water in a water-cooled pile is serious enough to necessitate jacketing the metal.

In order to determine whether hydrogen or the hydride
is formed, a tube was charged with cleaned uranium turnings
and placed in a furnace (11). An argon stream was bubbled
through cold water and passed through the tube. After sweep-
ing out the air, the uranium was heated to 250°, and the water
was warmed to about 70°. This permitted the water vapor carried
by the argon to come in contact with the uranium, which was
converted to a powder. The gas stream was shut off and the
temperature of the furnace raised to 500°. Copious amounts of
hydrogen were evolved, showing definitely that the hydride had
been formed, evidently from the hydrogen produced by the action
of steam on a part of the uranium.

E. Formation of Uranium Hydride by the Action

of Tetralin or Decalin on Uranium

At one time information was desired on the effect of
certain organic compounds on metallic uranium, with the possi-
ble aim of using these compounds as cooling agents for a pile
or related apparatus. A series of small flasks, each holding
a 2-3 gram lump of cleaned uranium, were charged with the
following reagents: biphenyl, naphthalene, diphenyl ether,
methyl alpha-naphthyl ether, tetralin, and decalin (13). The
air was flushed from the flasks with argon, and each was sealed
off at its neck. The flasks were heated to 210-270° for $2\frac{1}{2}$ to

SECRET

7 days, cooled, and the uranium lump cleaned and weighed. In

the case of the first four materials, the amount of attack was

negligible, ranging from 0.002 to 0.02 per cent of the total,

but in the tetralin and decalin flasks considerable black

powder was visible. The corrosion by the tetralin ($2\frac{1}{2}$ days)

amounted to 9.1 per cent of the total, while the decalin (7 days)

caused 3.1 per cent of the total to disintegrate.

The thermochemical calculations below show that it is very

likely that the attack of the uranium by the tetralin and decalin

is due to the formation of uranium hydride. Naphthalene would

be formed in each case. The equation for the reaction with

tetralin is:

$$3 \begin{array}{c} CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \end{array} + 4\ U \longrightarrow 3 \begin{array}{c} \end{array} + 4\ UH_3$$
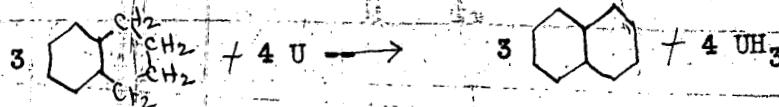
The energy change for the above reaction may be calculated as

follows: The bond and resonance energies for the organic com-

pounds are given by Wheland (14), and the heat of formation of

uranium hydride is taken from Part V (p. 29).

Reactants

3 x 4 = 12 C-H bonds = 12 x 87.3 = 1048	= 1048 Kg.-cal.
3 x 2 = 6 C-C bonds = 6 x 58.6	= 352
3 x resonance energy of tetralin = 3 x 41	= 123
Total	1523 Kg.-cal.

Products

3 x 2 = 6 C-C bonds = 6 x 100	= 600 Kg.-cal.
3 x 2 = 6 H-H bonds = 6 x 103.4	= 620
3 x resonance energy of naphthalene = 3 x 77	= 231
4 x heat of formation of UH_3 = 4 x 31	= 124
Total	1575 Kg.-cal.

Difference = 1575 - 1523 = 52 Kg.-cal.

SECRET

In these calculations the resonance energy of tetralin is assumed to be the same as that of benzene, although it may be a few kg.-cal. lower. It is seen that the occurrence of the reaction is favored thermally, 52 kg.-cal. being liberated by the reaction as written, or 17.3 kg.-cal. per mol of tetralin. A similar calculation may be made for the reaction with decalin.

F. The Composition of Uranium Hydride

1. Earliest Measurements

Two rapid experiments were run using small samples of uranium, which were weighed, converted to the hydride in short segments of glass tubing, and weighed again. The weight gains showed a hydrogen to uranium ratio of 4.15 and 3.85 (5), which suggested the formula UH_4, assuming that the hydride had a definite composition. The hydrogen used was not purified, the weight gains were not large, and the hydride samples were not protected from the air during weighing. Therefore more accurate analyses were made.

2. Analysis by Combustion

An apparatus was assembled for the preparation and oxidation of uranium hydride, the water formed being weighed (15). A sketch of the apparatus is given in Fig. 2. A Vycor combustion tube was placed in a hinged-top resistance furnace equipped with a variable transformer and a thermocouple with
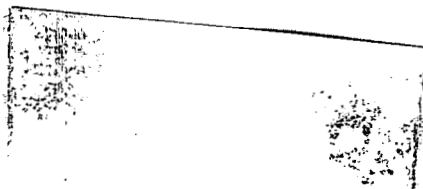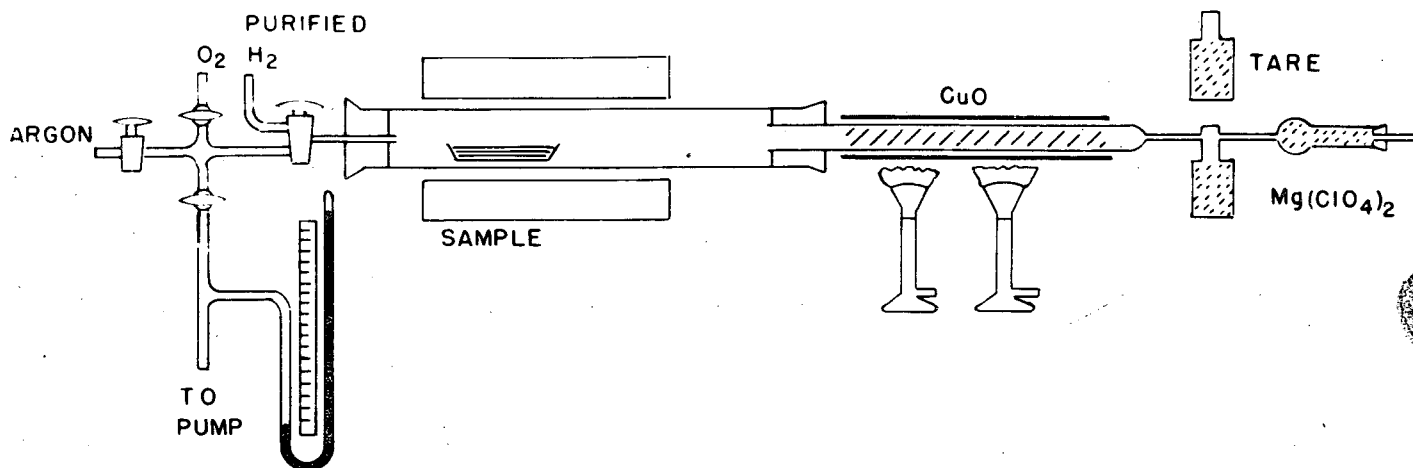
FIG. 2 APPARATUS FOR ANALYSIS OF UH$_3$ BY COMBUSTION

a potentiometer. Hydrogen, purified by passage over hot copper

followed by anhydrous magnesium perchlorate, was introduced

into the tube through one arm of a three-way stopcock, the other

arm of which was connected through stopcocks to an oxygen supply,

an argon supply, and a vacuum pump with a manometer, as shown

in Fig. 2. The other end of the combustion tube was connected

to a small quartz combustion tube packed with cupric oxide,

which could be heated with a flame. The exit of the small quartz

tube led to a magnesium perhhlorate-filled weighing tower. The

hydride was prepared and oxidized in a small quartz boat. About

seven grams of cleaned uranium turnings were used in each trial,

this giving approximately 800 mg. of water.

Hydrogen was passed through the apparatus and the furnace

was warmed to 250°. After complete conversion to the hydride,

the furnace was cooled, the hydrogen flushed out with argon,

and oxygen admitted. The oxidation was generally mild, some-

times without any glowing, but in several cases there were

small explosions, the quartz boat being moved and its contents

scattered, and the rubber stoppers being blown out. The small

tube holding the cupric oxide was kept hot during the oxidation

to insure converting any free hydrogen to water. In all cases

some hydrogen was liberated, as disclosed by the formation of

free copper; in a few trials the amount of hydrogen was so

great that the copper which was formed melted and broke the

tube. The oxidation was completed at 900°. Out of fourteen

attempts four were completed without mishap, giving the
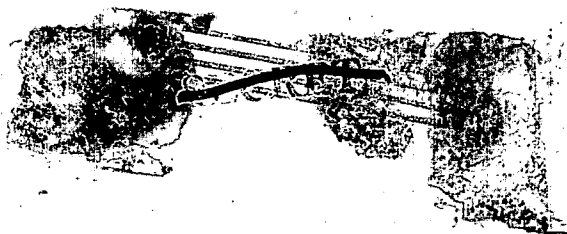
following H/U ratios: 2.94, 2.96, 2.96, 2.95. This showed that
the formula was most likely UH$_3$, and it also showed that on
this basis the hydride did not absorb additional hydrogen to
any extent, even though it had cooled to room temperature in
this gas.

In order to test the stability of uranium hydride, two
trials were run with one modification. After conversion to
the hydride, the hydrogen supply was shut off and the pressure
reduced to approximately 0.1 mm. The temperature was main-
tained at 256° ± 2° for 60 minutes, with the pump running.
Argon was then admitted, the system cooled, and the oxidation
carried out as usual. The amount of water formed showed that
the vacuum treatment at 256° had caused 54.6 per cent of the
hydride to decompose in the first trial, and 53.6 per cent in
the second (also see p. 85).

3. Analysis by Weight Gain and by Thermal Decomposition

Samples of uranium were converted to the hydride at 250°
in a small tube with stopcocks at either end (16). This per-
mitted a determination of the weight gain on formation, and
gave a H/U ratio of 3.04 in one trial and 2.97 in another.
The first is probably slightly in error, being to high. The
hydride samples were decomposed by heating to 400° under
vacuum until constant weight was attained. The loss in weight
gave an average H/U ratio of 2.95. In addition an apparatus
was constructed to determine the ratio by the volume of

hydrogen absorbed, and the volume of hydrogen evolved upon decomposition; these gave 2.92 and 2.94 respectively.

4. The Effect of Impurities on the Composition of Uranium Hydride

The analyses of uranium hydride have shown that the actual ratio of hydrogen to uranium is slightly less than three, namely about 2.97. This discrepancy cannot be entirely accounted for by experimental error. It has been found that the metal does not react with hydrogen if the uranium is a constituent of an intermetallic or other compound, and since quite complete analyses have been made of the uranium in use, it has proved possible (17) to calculate the effect of impurities. Table 1 gives a list of the major impurities in uranium and their abundance in a typical sample. The compound in which the impurity is most likely to be present is given, as well as its amount.

Table 1. Impurities in a Typical Sample of Uranium

Impurity	P. p. m. of Impurity	Present as	P. p. m. of Compound
C	300	UC	6100
Fe	60	U_6Fe	1550
Mn	5	U_6Mn	130
Si	50	USi	470
F	10	UF_3	50
O	80	UO	1240
N	30	UN	530
	Total p. p. m. of compounds		10070 or 1.007%

30-l-395

This means that 1.0 per cent of the material as weighed out

cannot combine with hydrogen. Thus if the free uranium com-

bines with hydrogen with a H/U ratio of exactly three, the

over-all ratio will be ninety-nine per cent of three, or

2.97. Since 2.97 is the determined ratio (within the limits

of experimental error and varying amounts of impurities),

it is certain that the formula of pure uranium hydride is

UH_3.

Other investigations have shown no substantial devi-

ation from this composition for uranium hydride formed under

pressures varying from 0.3 to 116 atmospheres (18) and under

temperatures varying from 150 to 330° (19).

IV. URANIUM DEUTERIDE[1]

It has been found that deuterium reacts with uranium

in the same way that hydrogen does (6, 13), forming a

deuteride with the same physical appearance as the hydride,

but with slightly different thermochemical properties (see

Part V). Attempts have been made to take advantage of these

differences to effect a separation of deuterium from hydrogen,

---

[1]
In this paper the term "hydrogen" is generally used to
denote protium (H^1) only, as distinguished from deuterium
(H^2).
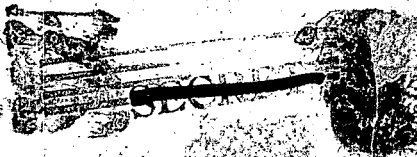
but none has proved practical. The properties of uranium

deuteride paralleled those of the hydride very closely.

Deuterium was conveniently prepared by passing heavy water

vapor over uranium turnings at 700° (20), when the follow-

ing reaction occurred quantitatively:

$$2 D_2O + U \longrightarrow 2 D_2 + UO_2$$
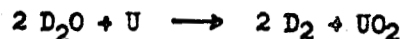
This process serves admirably to convert samples of ordinary

or heavy water into hydrogan or deuterium.

V. RESUME OF THE PHYSICAL PROPERTIES OF URANIUM
HYDRIDE AND DEUTERIDE[1] (6, 21)

A. Physical State

The particles of uranium hydride were found to be small

enough to pass through a 400 mesh sieve, which retained the

larger inclusions of impurities. But when prepared under

high pressures (as high as 126 atmospheres), the hydride

contained what appeared to be fibrous crystals, some 6 mm.

long, and was much coarser.

By x-ray diffraction studies the crystal structure of

uranium hydride has been found to be cubic. This structure

---

[1]
In addition to the writer, the following investigators
carried out most of the experimental work of this Part:
A. S. Newton, I. B. Johns, O. Johnson, A. Daane, R. W.
Nottorf, and R. E. Rundle.

is wholly unrelated to that of uranium metal, which is orthorhombic. The samples prepared under high pressure yielded x-ray diffraction patterns with much sharper lines than the low-pressure preparations, indicating considerable recrystallization. The patterns indicated only a single phase. X-ray analysis is particularly adapted to the distinction between compound formation and solid solution or interstitial compound behavior. The dissimilarity of the hydride structure to that of uranium is evidence that the system is not a solid solution. The x-ray data strongly suggest that uranium hydride is a true chemical compound.

The x-ray diffraction data showed that the unit cell of uranium hydride, which contains eight molecules, is 6.631 A on edge, while the corresponding lattice constant for uranium deuteride is 6.620 A. A diagram of the unit cell of the hydride is given in Fig. 3; only the uranium atoms are drawn in.

The bulk density of uranium hydride was determined as 3.4 g./cc. The particle density, measured by immersion in hexane, was roughly 11.4 g./cc., but more accurate determinations made using a helium densitometer (22) gave 10.95 ± 0.10 g./cc. Similar measurements with uranium deuteride showed that its density was 11.20 ± 0.1 g./cc. The x-ray densities of uranium hydride and deuteride were calculated as 10.92 ± 0.01 and 11.11 ± 0.01 g./cc. respectively. The density of

$\xleftarrow{\hspace{2cm}}$ 6.631 Å $\xrightarrow{\hspace{2cm}}$
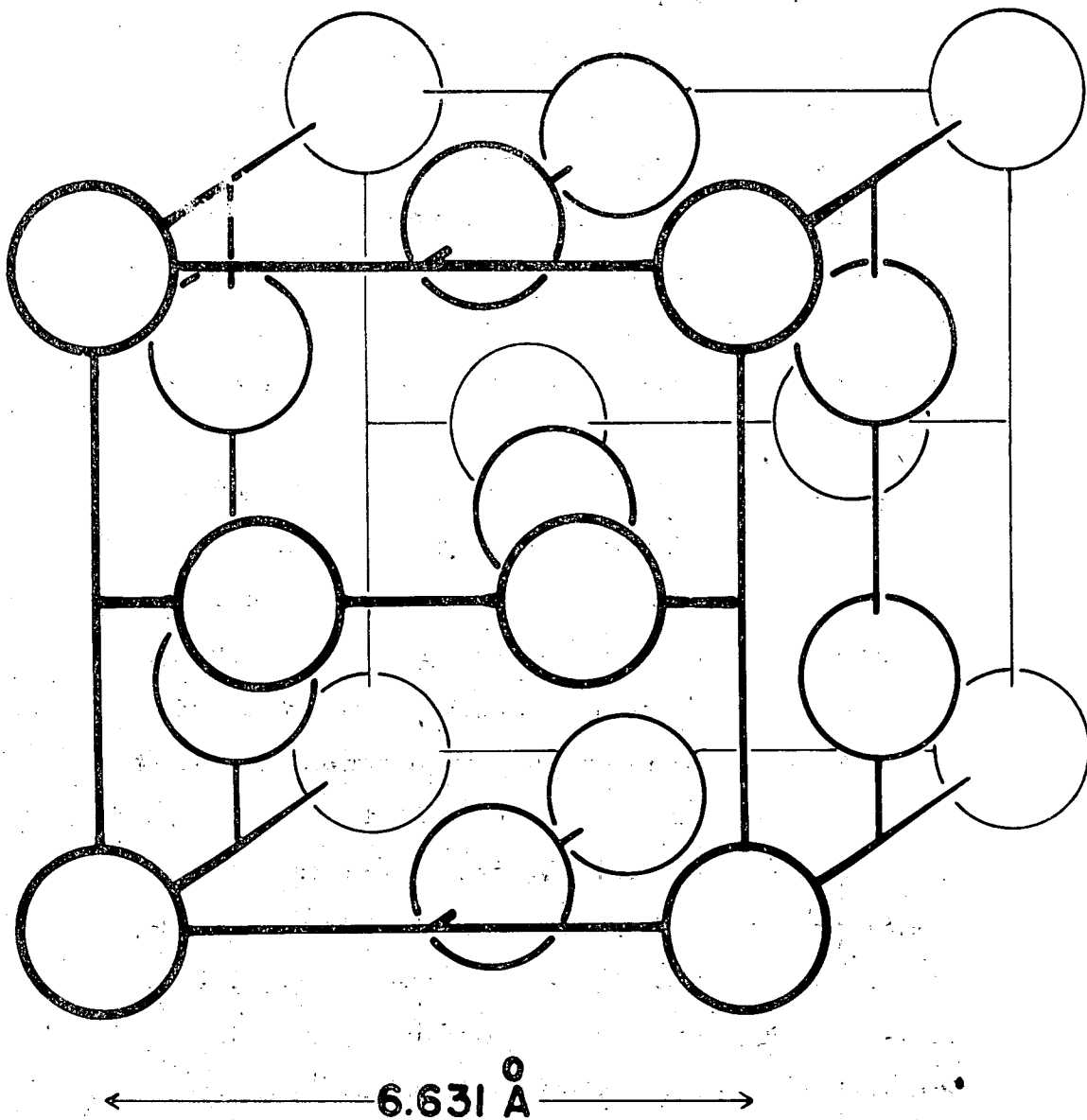
FIG. 3   THE STRUCTURE OF URANIUM HYDRIDE

34-l-295

uranium metal is 18.97 $\pm$ 0.05 g./cc. It is interesting to note that the density of the hydrogen alone in uranium hydride (0.14 g./cc.) is greater than the density in liquid hydrogen itself (0.07 g./cc.) by a factor of two.

When uranium hydride powder was compressed at pressures up to 22600 atmospheres, it formed blocks of metallic appearance with densities up to 8.7 g./cc. The coarse type of hydride which was prepared at high pressures could be compressed more than the ordinary form prepared at atmospheric pressure.

A series of measurements of the densities of uranium-uranium hydride and uranium-uranium deuteride mixtures was made using the helium densitometer. The purpose of these experiments was to determine whether there was any deviation from linearity in the volume-composition relationship. If the hydride were an imperfect solution of hydrogen in uranium, a deviation from linearity would be expected, whereas if two phases (a compound and unreacted uranium) or a perfect solid solution were present there should be no deviation. The result was that a plot of the specific volume (cc./g.) against composition was linear within the limits of error of the experiment ($\pm$ 1 per cent). The uranium-uranium deuteride behaved similarly.

B. Thermodynamic Properties

1. Pressure-Composition Isotherms

Extensive pressure-temperature-composition studies have
been made on the hydride. One of the chief difficulties en-
countered in obtaining accurate data on this aspect of the
investigation was the slowness with which equilibrium was
attained. Thus at constant temperature uranium metal pre-
pared by the decomposition of the hydride took on hydrogen
rapidly at the start, but on approaching the equilibrium
value the pressure changed very slowly, requiring as much as
two days to become constant.

The pressure-composition isotherms of the palladium-
hydrogen system is here reviewed briefly as a "normal" case.
The studies of Gillespie and Hall (23) show that at a
constant temperature pure palladium absorbs hydrogen as it
is introduced, the pressure rising steadily to a certain
value where it remains constant. This constant pressure,
whose magnitude depends upon the temperature, is maintained
until the composition corresponds to the formula Pd_2H,
when the pressure again rises. This is illustrated in
Fig. 4 for the 160° and the 180° isotherms. The substance
Pd_2H may be regarded as a compound, although its compo-
sition is not definite at the lower temperatures.

Isotherms for the uranium-hydrogen system were obtained
similarly, and they have the same general appearance. The

36-2-295
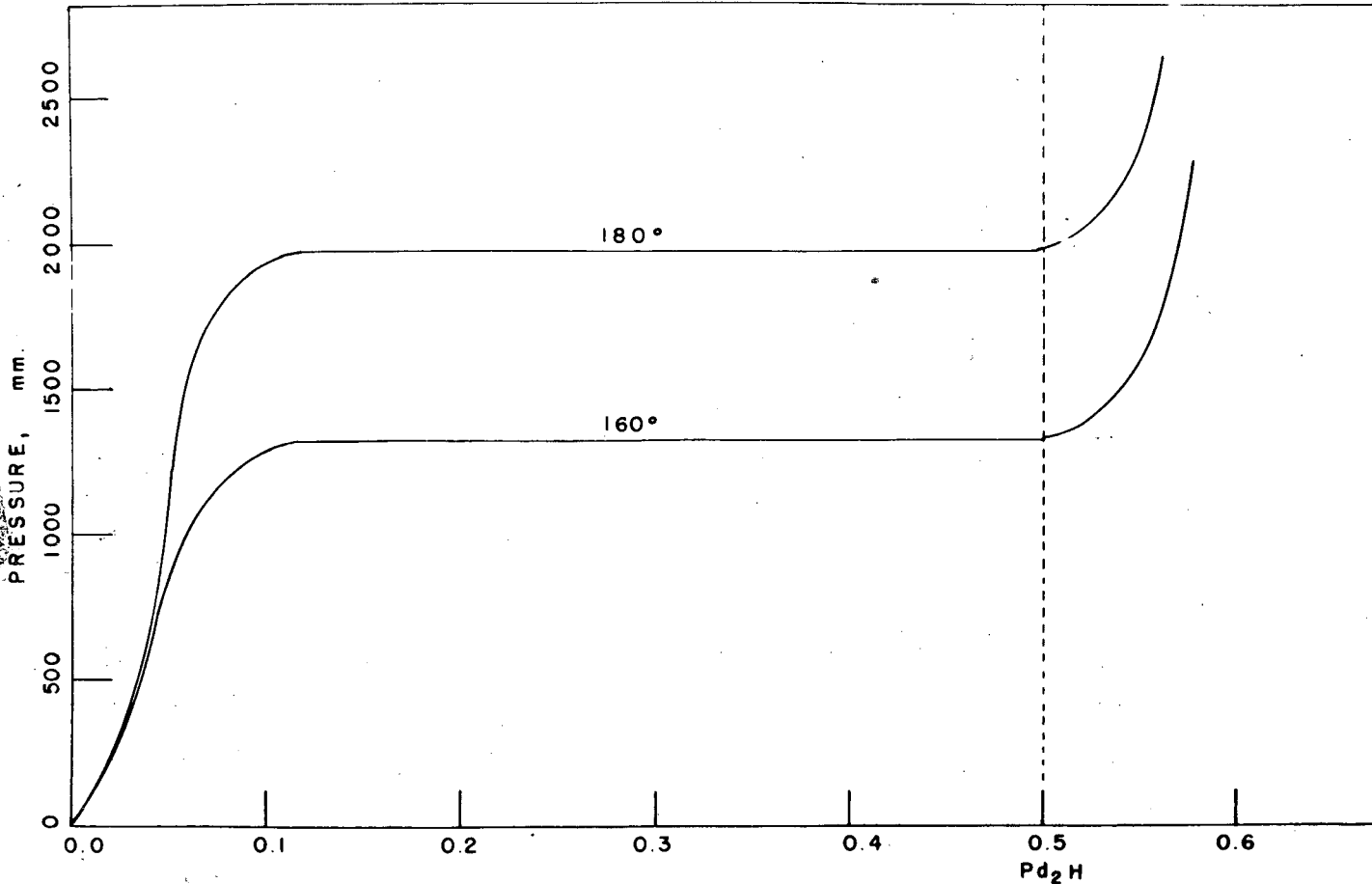
COMPOSITION — ATOMS OF H PER ATOM OF Pd

FIG. 4   THE PALLADIUM — HYDROGEN SYSTEM

357° isotherm is given in Fig. 5. The uranium hydride for
these experiments was held in a bulb surrounded by the vapors
of boiling mercury or other material, to insure constant
temperature. The manometer readings were taken after equi-
librium had been attained. Slightly different equilibrium
pressures were obtained, depending on whether the hydride
was being decomposed or formed; thus two curves were ob-
tained for each temperature. The higher curve was followed
on formation and the lower curve on decomposition. The
system is seen to be quite different from the palladium-
hydrogen system.

Another remarkable feature of the isotherm was a pro-
nounced dip in the lower curve in the region between 90 and
98 mol per cent UH_3. The dip was real and reproducible, and
appeared at both higher and lower temperatures. Samples of
composition near the bottom of the dip, when subjected to
x-ray analysis, showed the presence of uranium and uranium
hydride only. This unique behavior is as yet unexplained.

2. **Attempted Isothermal Transfer of Hydrogen from Uranium
Hydride to Powdered Uranium**

Two bulbs, one containing uranium hydride and the other
powdered uranium prepared by decomposing the hydride, were
heated side by side in the same bath to 325°, at which
temperature the dissociation pressure of the hydride is about
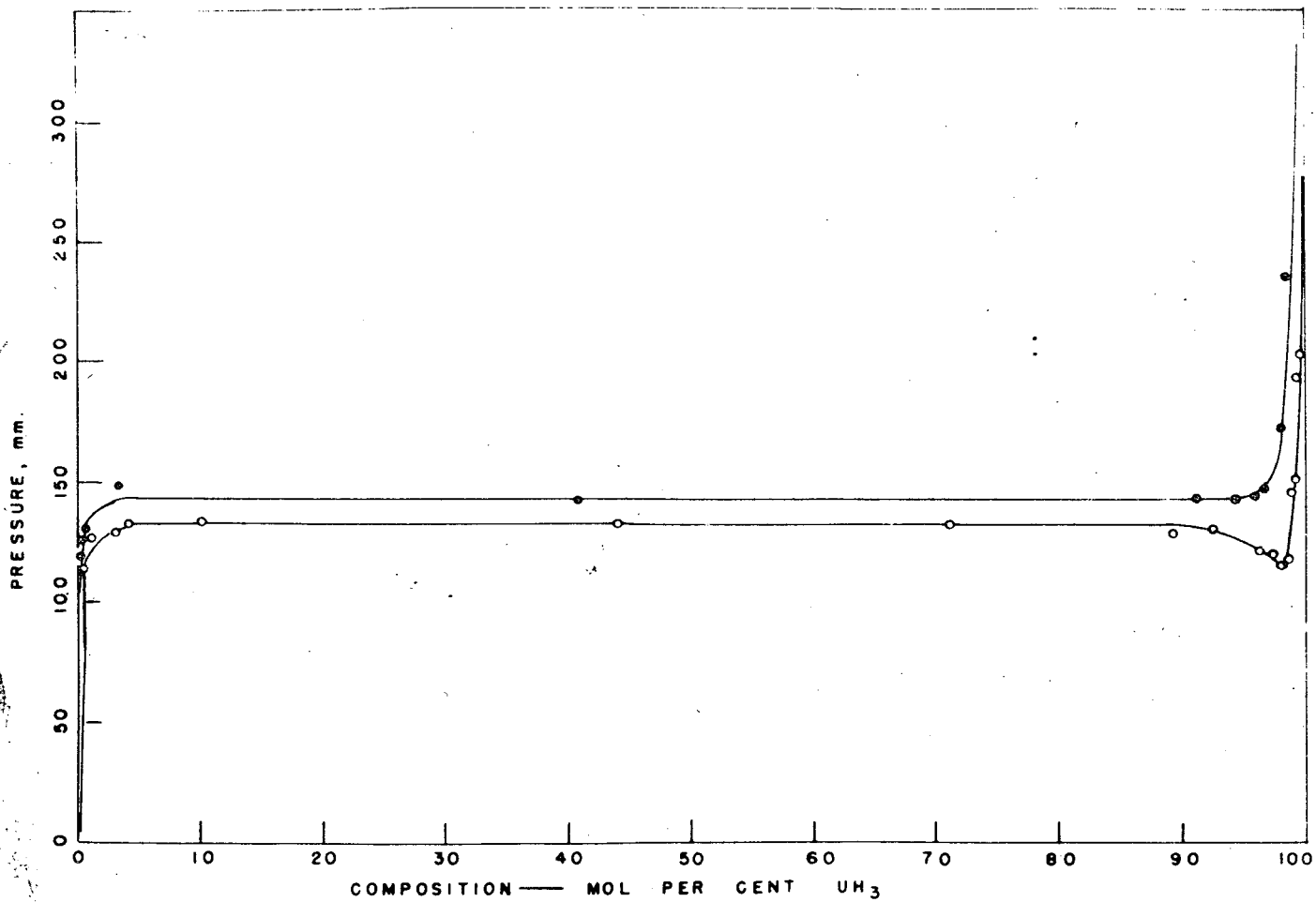
FIG. 5   URANIUM—HYDROGEN SYSTEM. THE 357° ISOTHERM

55 mm. The two bulbs were connected, and after ten hours

the bulb which held the powdered uranium was opened to a

vacuum system. Only a small amount of hydrogen was found,

and this could be accounted for by the volume of the bulb

and a hydrogen pressure of 55 mm. This evidence indicated

that uranium hydride does not consist of two hydrides of

different dissociation pressures, and is not a solid solution.

3. Dissociation Pressure-Temperature Studies

Samples of uranium hydride and deuteride, partially de-

composed into the metal, were allowed to come to equilibrium

with hydrogen or deuterium at a series of temperatures. The

dissociation pressure of the deuteride was about 1.4 times

that of the hydride over all the temperature range studied.

For example, at 357°, the dissociation pressure of the

hydride was 134 mm. and that of the deuteride 186 mm. Ac-

cording to the Clausius-Clapeyron equation, the logarithm

of the pressure is a linear function of the reciprocal of

the temperature. This was found to be the case, as shown

in Fig. 6, the slope of the hydride and deuteride curves

being identical. The equations of these lines are (pressure

in mm.):

Hydride $$\log p = \frac{-4500}{T} + 9.28$$

Deuteride $$\log p = \frac{-4500}{T} + 9.43$$
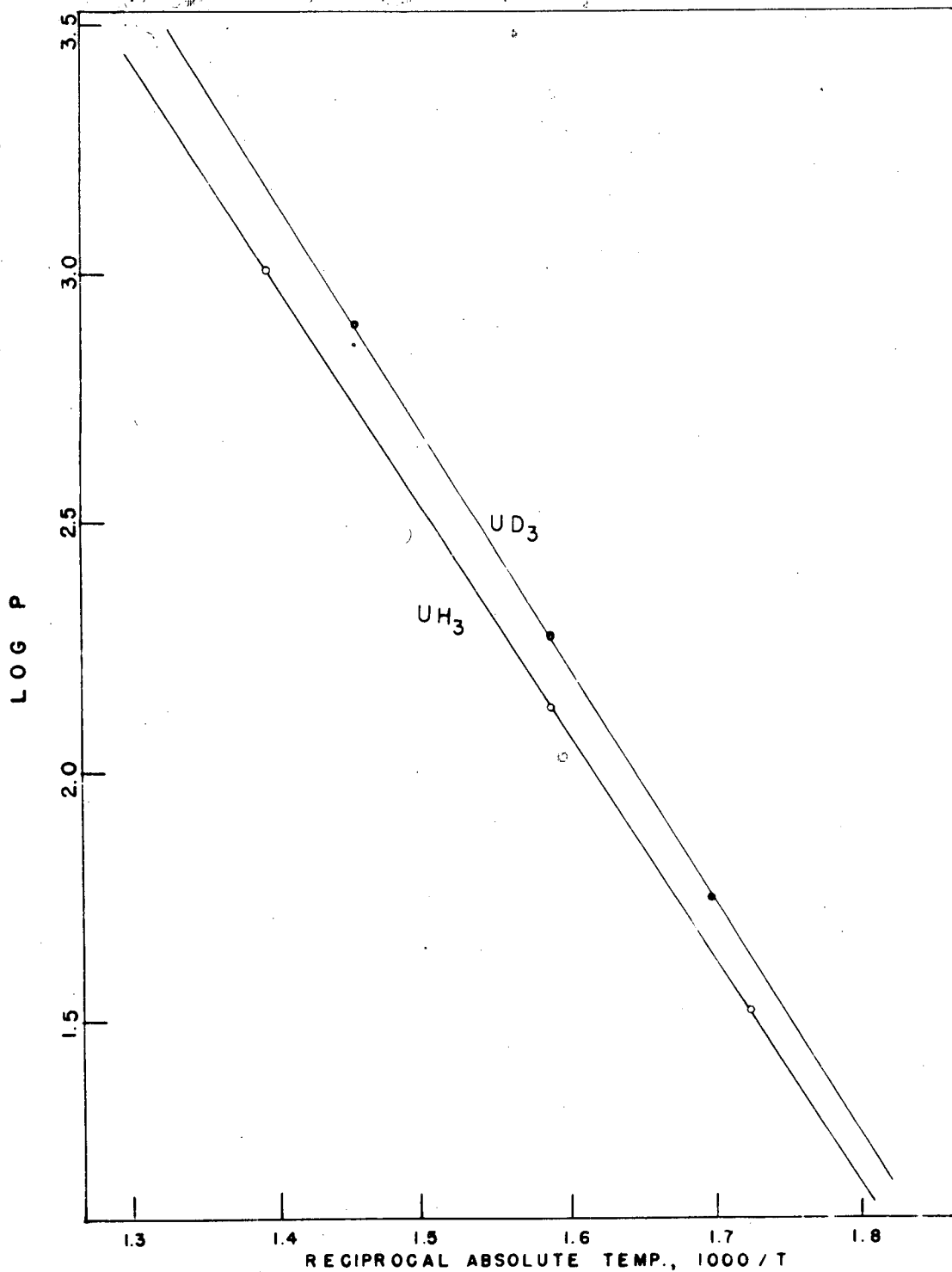
FIG. 6 LOGARITHM PRESSURE—RECIPROCAL TEMPERATURE
CURVES FOR UH₃ AND UD₃

4. Heat of Formation of Uranium Hydride

When the reaction forming the hydride is written

$$2 U + 3 H_2 \longrightarrow 2 UH_3$$
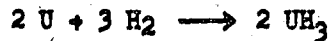
it is seen that the equilibrium constant is $k = p^{-3}$, where

p is the equilibrium hydrogen pressure. van't Hoff's re-

action isochore may be stated in the form

$$\frac{d \ln k}{d T} = \frac{\Delta H}{RT^2}$$

In this case

$$\frac{d \ln k}{d T} = \frac{-3 \, d \ln p}{dT}$$

Since $\quad \log p = \frac{-4500}{T} + 9.28,$

$$\frac{d \ln p}{d T} = \frac{2.3 \times 4500}{T^2} = \frac{-\Delta H}{3RT^2}$$

from which

$$\Delta H = {}^-61.6 \text{ Kg.-cal., or } \Delta H = {}^-30.8 \text{ Kg.-cal per mol}$$
of uranium

This value has been checked by direct measurement, using

uranium prepared by decomposing the hydride, since this form

of the metal reacts rapidly with hydrogen at room temperature.

The average value was $\Delta H = {}^-30.5$ Kg.-cal.

5. The Rate of Formation of Uranium Hydride and Deuteride

The rate of formation of uranium hydride depends upon

the temperature, the surface of the metal, the hydrogen

pressure, and the fraction of metal converted to the hydride.

At a constant temperature the reaction rate was found to decrease with decreasing pressure in a somewhat complicated fashion, in that the data indicated a 5/2 order of reaction. The kinetics of the reaction have been incompletely investigated and understood.

At the same temperature deuterium was observed to react with uranium at a rate only about one fifth that of hydrogen. This, and the different dissociation pressures of the hydride and deuteride, suggested a possible means of separating deuterium from hydrogen.

C. Hydrogen-Deuterium Separation Studies

A mixture of known composition of heavy and ordinary water was converted into a mixture of deuterium and hydrogen by reaction with uranium (p. 19), and this was converted into a mixture of uranium deuteride and hydride. The gas phase in equilibrium with the mixture was analyzed by the use of a density balance (24) capable of detecting a few tenths of a per cent of deuterium. It was found that there was rapid exchange at 300° between deuterium gas over uranium hydride, giving a mixture of hydride and deuteride.

In a typical experiment the uranium hydride-deuteride mixture contained 19.8 per cent deuteride. Ten samples of gas were withdrawn during thermal decomposition and each analyzed. The first contained 23.2 and the last 16.8 per

cent deuterium. These data correspond to a separation factor of 1.2, which shows relatively little enrichment.

A three meter electrically heated glass column was constructed and packed with uranium turnings, which were converted to the hydride and thermally decomposed. Hydrogen was passed up through the column at 250° in an attempt to use it as a fractionating column by taking advantage of the small separation factor. The first gas coming off was analyzed, but no enrichment of the small amount of deuterium in hydrogen could be detected. Modifications using uranium hydride amalgams (p. 81) were no more successful.

VI. THE CHEMICAL PROPERTIES OF URANIUM HYDRIDE

The data to this point have indicated that uranium hydride is best regarded as a true chemical compound, rather than a solid solution or interstitial compound, and thus would be expected to have chemical properties different from those of metallic uranium itself. In the reactions at elevated temperatures, however, there may be some doubt as to whether uranium hydride or the finely divided metal resulting from the decomposition of the hydride is the actual reactant. In low-temperature reactions, e.g. in aqueous solution, it is undoubtedly the hydride which reacts, while those which occur above about 350 or 400° are most probably reactions

of the metal. At the intermediate temperatures it is diffi-
cult to establish whether either or both components react.
At 250°, for example, the dissociation pressure of the
hydride is 4.8 mm., so that in a stream of a reacting gas
such as hydrogen chloride the exposure of a fresh uranium
surface would continually occur. In virtually all reactions
the same product is formed from the hydride or the metal in
any case. No attempt is made to distinguish the two cases
sharply, for even in those where it is known that the freshly
prepared powdered uranium is the reactant, the preparation
and decomposition of the hydride are an integral part in
the process.

In general uranium hydride reacts as a powerful reducing
agent, and often has an effect similar to that of uranium
metal, whose chemical properties have also been extensively
investigated (25). Since the investigations discussed below
were of a survey and exploratory character, only a few of
them were exhaustively studied.

A. Radiochemical Properties

As explained in the introduction, the finely sub-
divided character of the hydride immediately suggested
leaching of the fission products from the material prepared
from uranium from the piles. In order to investigate this,
a sample of uranium which had been subjected to a 53000-
micro-ampere hour deuteron bombardment in the St. Louis

cyclotron, and thus contained measurable amounts of the various fission products, was converted to the hydride and divided into two weighed portions (26). The first was refluxed with 0.5 N hydrochloric acid, and the second with 5 N hydrochloric acid containing small amounts of KI and the chlorides of the following metals as carriers: Te, Mo, La, Y, Zr, Ce, Ba, Sr, and Th. Vycor flasks were employed to minimize adsorption. The solutions acquired a deeper and deeper green color as the refluxing continued. Aliquots of the first solution were taken periodically, centrifuged, and evaporated to dryness on a watch glass. The total radioactivity was measured using a Lauritsen electroscope. Aliquots from the second solution, containing the carriers, were also taken, and analyzed by chemical separations (27). The uranium in all aliquots was determined. The results showed that no preferential extraction of any element occurred, and that the activities of the solutions were in proportion to the amount of uranium they contained. It thus became evident that the fission products were dissolved only when the uranium hydride in which they were held was also dissolved, and no enrichment could be achieved.

Further experiments[1] were conducted on the behavior of the fission-produced xenon in uranium when the metal is

---

[1] The remainder of the radiochemical studies were carried out by J. A. Ayres and I. B. Johns.

46-1-295

converted to its hydride (28). Among the fission products present in neutron-bombarded uranium are three short-lived isotopes of krypton, which were allowed to decay before the experiments were made, and two iodine isotopes, which disintegrate into xenon isotopes of 9.3 hour and 5.3 day half lives.

An apparatus was constructed which consisted of a reaction flask leading to a bead tube containing saturated sodium bisulfite; this was connected through a trap to a heated cupric oxide-packed tube. The exit of the cupric oxide tube led to a eudiometer filled with potassium hydroxide solution. The top of the eudiometer was connected to a tube holding a Geiger-Mueller counter tube.

Samples of bombarded uranium were converted to the hydride in the reaction flask. Any radioactive iodine carried by the excess hydrogen was absorbed in the sodium bisulfite tube, and the excess hydrogen was converted to water by the hot copper oxide. A small amount of argon was introduced along with the hydrogen into the reaction flask, so as to provide a carrier for any traces of radioactive xenon liberated. The gas was caught in the eudiometer and then flushed into the counter tube, and any activity measured. Next the uranium hydride in the reaction flask was decomposed at 400° under reduced pressure. The gases evolved were again collected and the radioactivity measured. Finally the remaining

metal (in some cases re-converted to the hydride) was completely dissolved in phosphoric acid, and the apparatus flushed with carbon dioxide, which dissolved in the alkali of the eudiometer. This permitted the calculation of the total xenon radioactivity.

The studies showed that the disintegration of the metallic structure of the uranium upon conversion to the hydride caused less than one per cent of the xenon to be liberated. Even on thermally decomposing the hydride less than 15 per cent of the xenon was given up. Complete solution of the sample was necessary to cause the evolution of all of the xenon. It is not entirely clear why the trace xenon clings so tenaciously to the uranium or its hydride, but it is in keeping with the retention of the fission products by the hydride upon leaching. Uranium hydride prepared in the presence of some radioactive xenon failed to adsorb the gas. Experiments on the behavior of the radioactive xenon in uranium hydride amalgams are discussed in Part VII (p. 68).

B. Action of Air, Nitrogen, Carbon Dioxide, and Water (13)

1. Air and Oxygen

The pyrophoric nature of the hydride has already been mentioned. When the hydride is burned water and uranium oxide, U_3O_8, are formed. The reaction was not found explosive even when as much as 1500 g. was burned in the open

air. Numerous samples of the hydride were not pyrophoric,

and it was found that if a preparation was exposed to small

amounts of air at a time over an hour or so it could then

be handled in air without catching fire, although it was not

completely air-stable. Evidently a protective layer of oxide

formed on each particle. When a sample was so treated, peri-

odic weighings showed that it was slowly being oxidized on

standing in the air, the rate falling to about half its origi-

nal value in 45 days. When handling uranium hydride in the

laboratory, it is recommended that the operator take the pre-

caution of wearing asbestos gloves and a face shield.

Oxygen acts similarly to air, but more vigorously. It

was mentioned earlier (p. 15) in connection with the analysis

of the hydride by combustion in oxygen, that some cases of

oxidation without ignition had been observed.

2. Nitrogen and Carbon Dioxide

For the handling and transfer of uranium hydride, a

"dry box" was often used, from which the air was flushed

with nitrogen, carbon dioxide, or in some small boxes, with

helium or argon. The experience was that the hydride could

be handled safely in either nitrogen or carbon dioxide if

care was taken to flush all the air from the box. When

enough air was left in the box to ignite the hydride, it

continued to burn in either nitrogen or carbon dioxide,

forming uranium nitride or oxide. These reactions are
further discussed in Section F (p. 53).

3. Water

It was observed that small quantities of the hydride
(1-30 g.) could be covered with water with no apparent
reaction; the odor of acetylene was detected, evidently
from the carbide impurities. On the other hand, when a
larger quantity (500-600 g.) of the hydride was wetted,
adding the water all at once, the mass deflagrated, the
sudden red heat breaking open the glass containers. Uranium
oxide was formed, and hydrogen was liberated by the reaction.

When water was added dropwise to a large amount (400 g.)
of the hydride in a flask, a small amount of heat was given
off. The rate of addition of the water was adjusted so as
to permit the heat to be dissipated. In this fashion the
whole mass was thoroughly wetted without accident. The
reaction of uranium hydride with steam is discussed in
Section F (p. 52).

C. Action of Acids, Oxidizing Agents, and Bases (13)

1. Non-oxidizing Acids

Hydrochloric acid, dilute or concentrated, hot or cold,
reacted only very slowly with uranium hydride. The solutions
took on a green color as uranous chloride was formed and hydro-
gen was liberated. Uranium metal, even in the massive form,

reacted with hydrochloric acid with phenomenal rapidity.
The effects of dilute sulfuric, perchloric, and phosphoric
acids were similar to that of hydrochloric. The solution
rate in hot concentrated phosphoric was quite high.

There was no reaction between the hydride and dilute
acetic acid, but on boiling under reflux a brownish-black
apparently colloidal suspension resulted. The hydride sus-
pension readily passed through filter paper but some solid
was thrown down by long centrifuging. The hydride did not
react with glacial acetic acid until some hydrogen chloride
gas was bubbled into the suspension. This caused a vigorous,
exothermic reaction, and upon cooling a light green precipi-
tate was deposited, which by analysis (Part IX) was shown
to be uranous acetate (29). The reaction of acetic acid
vapor at elevated temperatures is considered later (p. 54).

2. Common Oxidizing Agents (13)

Nitric acid, either dilute or concentrated, was found
to attack the hydride violently, evolving the oxides of
nitrogen, and forming a yellow solution of uranyl nitrate.
On several occasions the concentrated acid caused ignition.

Concentrated sulfuric acid, when heated with uranium
hydride, was readily reduced to sulfur dioxide, sulfur, and
hydrogen sulfide.

Uranium hydride was attacked by thirty per cent hydrogen
peroxide, emitting sparks. The product was an oxide of

uranium. In the presence of non-oxidizing acids, hydrogen peroxide caused rapid solution of the hydride to form the uranyl salt of the acid. This affords a preparative means for uranyl salts. For example, with sulfuric acid, uranyl sulfate was formed. Organic acids, such as acetic, oxalic, tartaric, and citric acids, did not alone attack uranium hydride, but with hydrogen peroxide the uranyl salts of these acids were formed. Equations for two of the above processes are:

$$2 \text{ UH}_3 + 9 \text{ H}_2\text{O}_2 + 2 \text{ H}_2\text{SO}_4 \longrightarrow 2 \text{ UO}_2\text{SO}_4 + 14 \text{ H}_2\text{O}$$
$$\text{uranyl sulfate}$$

$$2 \text{ UH}_3 + 9 \text{ H}_2\text{O}_2 + 2 \text{ H}_2\text{C}_4\text{H}_4\text{O}_6 \longrightarrow 2 \text{ UO}_2\text{C}_4\text{H}_4\text{O}_6 + 14 \text{ H}_2\text{O}$$
$$\text{uranyl tartrate}$$
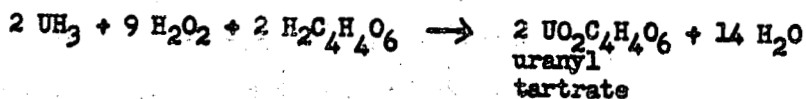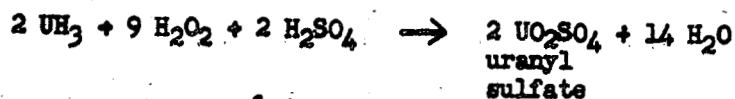
When an excess of hydrogen peroxide was added, peruranic acid, $UO_4 \cdot 2H_2O$, was precipitated.

Strong oxidizing agents, with dilute sulfuric acid, rapidly dissolved uranium hydride. These included ceric sulfate, potassium dichromate, permanganate, bromate, and chlorate. Sodium hypochlorite alone had no effect; such solutions are slightly alkaline.

3. Bases

Aqueous solutions of sodium, potassium, and ammonium hydroxides had no visible effect on the hydride. Sodium cyanide, whose solutions are caustic, also failed to react.

D. Action of Solvents (13)

When samples of uranium hydride were covered with a series of solvents, the only visible effect was the evolution of very small bubbles for a few hours. The bubbles may have been adsorbed hydrogen. The solvents included benzene, toluene, hexane, ether, ethanol, dioxane, ethyl acetate, amyl acetate, carbon disulfide, glacial acetic acid, and acetone.

With the first trial carbon tetrachloride behaved as the solvents above, but on a second a quite violent explosion occurred. A third trial with a smaller quantity of the solvent caused a red glow on contact with the hydride. Carbon was a visible product of each reaction, and hydrogen and uranium chlorides were probably the others. The reaction of uranium hydride with carbon tetrachloride vapor is given in Section F (p. 50). Addition of chloroform and chlorobenzene to uranium hydride samples evolved more gas than solvents such as benzene did, and a slight odor of hydrogen chloride was detected. No violent reaction took place.

Liquid ammonia had no effect on the hydride. Mercury appeared to form an amalgam, which is discussed separately (Part VII).

53-2-295

E. Action of Metallic Salts (15)

1. Silver Salts

a. <u>The reactions with silver salts</u>[1]. Silver salts in
general were found to react rapidly with uranium hydride
yielding free silver and a uranyl salt. Silver fluoride,
which is very soluble in water, reacted exothermally with
the hydride, but since uranium tetrafluoride is insoluble
the metal was not oxidized beyond the tetravalent stage.
Some hydrogen was liberated, and it is probable that the
main reaction can be written as follows:

$$2 \ UH_3 + 8 \ AgF \longrightarrow 2 \ UF_4 + 8 \ Ag + 3 \ H_2$$
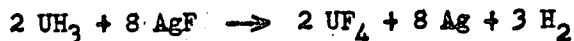
It is also possible that to some extent the following re-
action occurred:

$$UH_3 + 7 \ AgF \longrightarrow UF_4 + 7 \ Ag + 3 \ HF$$

Solutions of silver nitrate reacted readily, dissolving
the uranium hydride, liberating silver and hydrogen, and
forming a yellow solution. The equation for the most proba-
ble principal reaction is:

$$2 \ UH_3 + 12 \ AgNO_3 + 2H_2O \longrightarrow 12 \ Ag + 2 \ UO_2(NO_3)_2 +$$
$$8 \ HNO_3 + 3 \ H_2$$
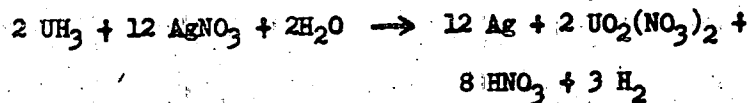
which leads to the belief that six moles of silver were
liberated for each mole of uranium hydride consumed. In

---

[1]
 The reactions of uranium hydride with silver salts and most
of the other heavy metal salts were investigated for the
greater part by J. A. Ayres.

order to test this, known weights of uranium were converted
to the hydride and treated with an excess of silver nitrate;
the silver formed was filtered off, washed, ignited and
weighed. It was found that the average number of mols of
silver liberated per mol of uranium hydride was 5.8, and
this is easily explainable on the basis that the nitric
acid formed during the reaction oxidized part of the urani-
um hydride as follows:

$$UH_3 + 5 HNO_3 \longrightarrow 3 NO + UO_2(NO_3)_2 + 4 H_2O$$
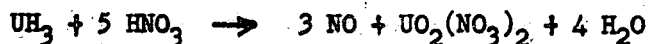
Whereas silver fluoride and nitrate oxidized uranium
hydride rapidly, requiring only a few minutes to consume a
gram or two, the less soluble silver salts were much more
sluggish in their action. Thus silver sulfate, acetate,
and tartrate solutions required four to twenty hours to
dissolve gram quantities of the hydride.

Silver perchlorate, however, is exceedingly soluble,
and reacted with the hydride particularly rapidly. This
reagent also dissolves uranium metal rapidly, and this re-
action has been studied in some detail (30). It was found
that contrary to expectations, that some of the perchlorate
ion itself was reduced and precipitated as silver chloride.
From analogy, the two principal reactions with uranium
hydride may be represented:

$$2 \, UH_3 + 12 \, AgClO_4 + 4 \, H_2O \longrightarrow 12 \, Ag + 2 \, UO_2(ClO_4)_2 +$$
$$8 \, HClO_4 + 3 \, H_2$$

$$2 \, UH_3 + 5 \, AgClO_4 \longrightarrow 4 \, Ag + AgCl + 2 \, UO_2(ClO_4)_2 + 3 \, H_2$$
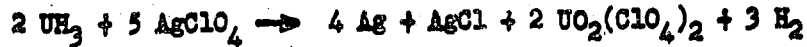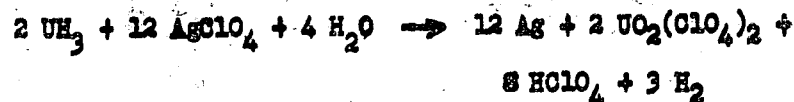
The silver-silver chloride mixture formed by the action of either the metal or its hydride on silver perchlorate separated as gray, spongy masses.

Silver perchlorate is abundantly soluble in toluene (31), and it was observed that even in this non-aqueous medium a rapid, exothermic reaction with the hydride ensued (32). It was hoped to find a reaction in which the amount of silver liberated was equivalent to the amount of free uranium (as the hydride) present, in order that the silver could be filtered off and weighed, this operation serving as an analytical method for the determination of elemental uranium. It was proved, however, that again a mixture of silver and silver chloride was formed, and the reaction was not adaptable to analytical work. A possible equation is:

$$2 \, UH_3 + 6 \, AgClO_4 \longrightarrow 2 \, Ag + 2 \, AgCl + Ag_2O +$$
$$2 \, UO_2(ClO_4)_2 + 3 \, H_2O$$
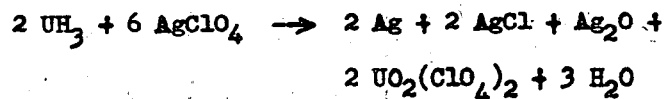
It may be that these reactions would be useful in analyses for the perchlorate ion. Treatment with an excess of uranium or uranium hydride may reduce the perchlorate quantitatively to chloride, which could be determined by the ordinary methods.

b. Preparation of uranyl salts. A means of preparing pure solutions of uranyl salts from the corresponding silver

salts is suggested by the above reactions. An excess of uranium hydride would be employed, with silver oxide added to neutralize the acids formed. The unchanged hydride, silver oxide, and silver would be filtered off, and the filtrate would contain the pure uranyl salt. The equations below illustrate the reactions:

$$2 \ Ag_2SiF_6 + 2 \ UH_3 + 4 \ Ag_2O \longrightarrow 2 \ UO_2SiF_6 + 12 \ Ag + 3 \ H_2$$
$$\text{uranyl fluosilicate}$$

$$2 \ Ag_2C_3H_5O_3 + 2 \ UH_3 + 4 \ Ag_2O \longrightarrow 2 \ UO_2C_3H_5O_3 + 12 \ Ag$$
$$\text{uranyl lactate}$$
$$+ 3 \ H_2$$
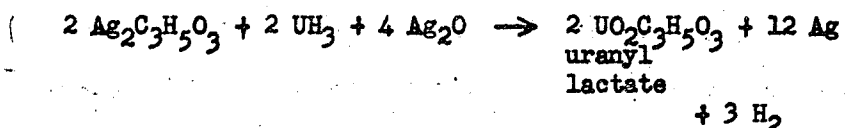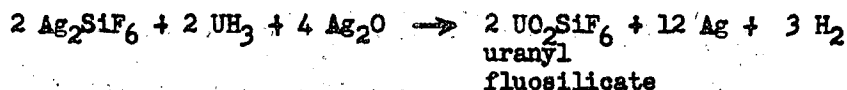
A solution of uranyl salicylate was prepared in this fashion by heating a suspension of salicylic acid, silver oxide, and uranium hydride. The filtrate contained 1.4 mg. of uranium per 100 ml. presumably as the salicylate. The usefulness of this reaction could probably be extended by further investigations.

2. Other Heavy Metal Salts

A number of other heavy metal salt solutions were also found to react with uranium hydride. The action of the salts of copper, mercury, lead, tin, arsenic, antimony, bismuth and iron were briefly investigated.

Cupric sulfate solutions failed to react with the hydride at room temperature, but on boiling, a slow reaction took place as evidenced by the formation of copper. A solution of cupric ammonium chloride, which dissolves metallic

iron rapidly without formation of a precipitate (33), was
found to react with uranium hydride violently, causing com-
plete solution. The copper was reduced to the cuprous
state, forming a soluble complex with the ammonium chloride.

Mercuric chloride solution gave a rapid reaction,
forming a gray precipitate, probably a mixture of mercury
and mercurous chloride. Mercuric nitrate also reacted,
yielding some free mercury.

Arsenic trichloride solution was found to react very
slowly at 100°, while antimony trichloride in 3 N hydrochloric
acid liberated free antimony in an exothermic reaction.

Ferric sulfate containing a little sulfuric acid dis-
solved the hydride slowly but smoothly at the boiling point.

F. The Reactions of Various Gases with Uranium Hydride;

   The Preparation of Tri- and Tetravalent Uranium Salts

It has been found possible to prepare a number of tri-
and tetravalent uranium compounds conveniently by passing
certain gasses over the hydride at temperatures varying
from room temperature to 500°, depending upon the specific
reaction. A dry state may be maintained by this means,
and in no case is it necessary to exceed the melting point
of the product, giving an anhydrous, fine, and easily-
handled powder rather than a fused mass. Only simple appa-
ratus is required; a typical set-up is shown in Fig. 7. In
general the methods are far superior to the older procedures.

58-l-295

HYDROGEN

→

OTHER
GAS

BOAT HOLDING
URANIUM HYDRIDE

EXHAUST
GASES

→
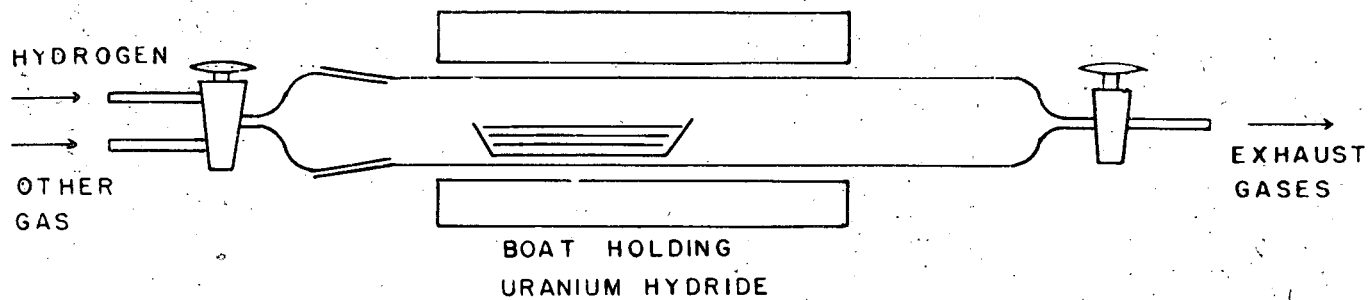
FIG. 7   APPARATUS FOR   PREPARATION OF URANIUM   COMPOUNDS   FROM UH_3

1. Preparation of Uranium Halides[1]

a. <u>Uranium tetrafluoride</u>. Anhydrous hydrogen fluoride was found to react smoothly with uranium hydride at any temperature ranging from room temperature to $400°$ (13). Monel and nickel apparatus were used. The product was a light green powder and analysis (analytical methods are given in Part IX) showed fair conformity with the composition of uranium tetrafluoride, as follows:

	Calculated for UF_4	Found
U	75.8%	75.5%
F	24.21	23.91

The equation is:

$$2\ UH_3 + 8\ HF \longrightarrow 2\ UF_4 + 7\ H_2$$
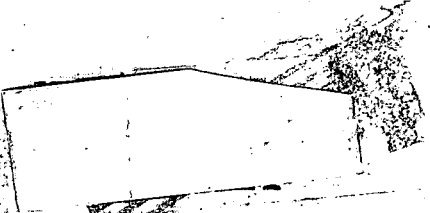
A series of hydrofluorination experiments with large quantities of uranium was carried out (34). In an agitated apparatus, the hydride reacted rapidly, 92 per cent of an 1160 gram sample being converted within two hours. It was not found necessary to convert all of the metal to the hydride before introducing the hydrogen fluoride: Hydrogen and hydrogen fluoride reacted simultaneously. Careful temperature control was essential.

---

[1] The reactions of uranium hydride with halogen-bearing gases were for the most part investigated by A. S. Newton, O. Johnson, and R. W. Nottorf.

b. **Uranium tri- and tetrachloride.** Anhydrous hydrogen chloride was observed to react with uranium hydride at 250° to give a reddish-brown powder, which changed to an olive-green color on cooling (13). The hydride prepared from 262 g. of uranium was treated with hydrogen chloride, and the product obtained weighed 375 g., whereas the conversion to uranium trichloride, UCl_3, would yield 379 g. Analysis of the product showed conformity with the composition of uranium trichloride:

	Calculated for UCl_3	Found
U	69.0%	69.2%
Cl	31.0	29.4

Uranium trichloride was prepared by this reaction on a number of occasions, and it was noticed that a small amount of a white crystalline sublimate formed on the cooler regions of the reaction tube just beyond the position of the uranium trichloride (35). A bit of this volatile material gave a negative test for uranium, but positive tests for chloride ions. It was found that the amount of white sublimate was increased if the uranium hydride was exposed to air before reaction with the hydrogen chloride. This strongly suggested that ammonium chloride was being produced by the action of hydrogen chloride on a uranium nitride. In fact, when some pure uranium nitride was treated with hydrogen chloride at elevated temperatures, copious quantities of ammonium chloride

were sublimed away, and condensed on the cooler parts of the apparatus.

Chlorine was passed over uranium hydride, and the violent reaction that took place was uncontrollable, and a molten product was formed. The chlorine was then diluted with ten volumes of helium and the reaction was then relatively smooth at 250°. A light green powder was formed, which was essentially uranium tetrachloride, UCl_4, as was shown by the following analysis:

	Calculated for UCl_4	Found
U	62.6%	63.6%
Cl	37.4	37.5

A more convenient method of preparing uranium tetrachloride was found by preparing the trichloride first, and then passing chlorine over it, as follows:

$$UH_3 + 3\ HCl \longrightarrow UCl_3 + 3\ H_2$$
$$2\ UCl_3 + Cl_2 \longrightarrow 2\ UCl_4$$
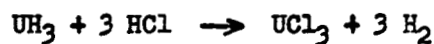
The product was a yellow-green hygroscopic powder which on analysis showed the following composition:

	Calculated for UCl_4	Found
U	62.6%	63.6%
Cl	37.4	36.4

Mixed uranium halides were prepared by passing bromine or iodine vapors over uranium trichloride (36). Thus uranium monobromotrichloride, $UBrCl_3$, was made as a tan

62-l-295

powder by the action of bromine at 250°. An x-ray diffraction pattern of this material was indistinguishable from the pattern of a substance made by melting together one mol of uranium tetrabromide and three of the tetrachloride. This and additional evidence suggested that the system UCl_4-UBr_4 forms solid solutions. The mixed iodide, $UICl_3$, was a dark tan powder, which upon heating was decomposed into iodine and uranium trichloride.

The reactions of uranium hydride with two other chlorine-containing gases were also investigated. Carbonyl chloride and carbon tetrachloride vapor reacted smoothly at 250°, although neither reacts appreciably with uranium turnings below 500°. The products from the hydride in both cases were contaminated with carbon or a carbide, and probably were mostly the tetrachloride. Possible principal reactions are:

$$2\ UH_3 + 4\ COCl_2 \longrightarrow 2\ UCl_4 + 3\ H_2 + 4\ CO$$

$$2\ UH_3 + 2\ CCl_4 \longrightarrow 2\ UCl_4 + 3\ H_2 + 2\ C$$
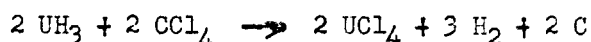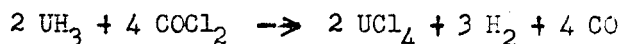
c. <u>Uranium tri- and tetrabromide.</u> Reactions analogous to those with chlorine-containing gases were observed (13). Uranium hydride prepared from 392 g. of uranium was treated with hydrogen bromide at 300° until the reaction vessel was at constant weight (20 hours). The product weighed 781 g., whereas 782 g. was calculated on the basis of conversion to uranium tribromide. Analysis showed close correspondence to
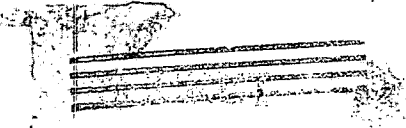
the composition predicted:

	Calculated for UBr$_3$	Found
U	49.9%	50.1%
Br	50.1	49.9

The uranium tribromide was a reddish-brown powder.

The reaction of bromine itself was examined by employing helium as a carrier gas. The reaction was quiet at 350°, yielding a light brown powder, which by analysis was shown to have the composition corresponding to the tetrabromide:

	Calculated for UBr$_4$	Found
U	42.7%	42.7%
Br	57.3	57.2

Uranium tetrabromide was also prepared by brominating the tribromide; this constitutes the preferred procedure. The product analyzed as follows:

	Calculated for UBr$_4$	Found
U	42.7%	42.4%
Br	57.3	56.9

Uranium monoiodotribromide, UIBr$_3$, was made by the iodination of the tribromide (36). It was a dark brown hygroscopic powder.

d. Uranium iodides. The status of the uranium iodides is less satisfactory than that of the other halides. The products were found to be thermally unstable and to decompose on standing, especially after being exposed to the air (13). Iodine vapor, carried by helium, was found to react readily
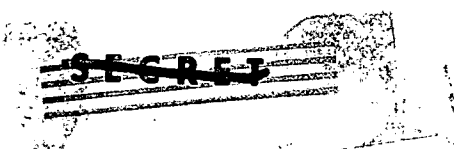
with uranium hydride forming a brown product. Hydrogen iodide at 250-400° gave a similar product. Analyses were uncertain, but the products were probably uranium tri- or tetraiodide or mixtures of these materials.

The effect of another iodine-bearing material was tested, namely methyl iodide (37). The vapors carried by hydrogen were passed over uranium hydride at 275-300°. A brown product was formed, whose uranium content was found to be 39.0 per cent, which is reasonably close to the uranium content of the triiodide, UI_3, which is 38.5 per cent. The material was ignited by air, when fumes of iodine vapor were liberated.

2. Uranium Oxide, Sulfide, Nitride and Phosphide (13)

When steam was drawn over uranium hydride prepared from a known amount of uranium, the mass glowed, and after completion of the reaction, a brown powder remained. The weight change showed the product to be uranium dioxide, formed as follows:

$$2 \; UH_3 + 4 \; H_2O \longrightarrow 2 \; UO_2 + 7 \; H_2$$

The reaction between hydrogen sulfide and uranium hydride was investigated. Little reaction was observed up to about 400°, when the reaction mass increased in volume and formed a fine black powder. Uranium hydride prepared from 10.03 g. of the metal yielded 12.61 g. of the sulfide,

which corresponded to an S/U ratio of 1.93. The product was therefore most probably uranium disulfide, US_2.

Uranium hydride was found to react fairly rapidly at 250° with either nitrogen or ammonia, yielding a gray product. The weight gains showed both preparations to have compositions lying between U_2N_3 and UN_2, which, as a study of the uranium-nitrogen system (38) has shown, is within a continuous phase region.

Phosphine was passed over the hydride made from 2.35 g. of uranium until the weight was constant. The temperature was 400°. The dark gray powder formed weighed 2.83 g., which corresponds to a P/U ratio of 1.55, and the phosphide was most probably the sesqui-phosphide, U_2P_3.

3. Reactions with Other Gases and Vapors

The action of carbon dioxide on uranium hydride was found to be very slow but appreciable at room temperature, with the rate steadily increasing with the temperature (13). Above about 300°, the reaction was quite rapid. The products were probably uranium dioxide, and carbon or a uranium carbide.

The action of carbon monoxide was much slower. It behaved more or less as an inert gas and uranium hydride was decomposed to the metal. This was discovered in an attempt to prepare uranium carbonyl by the action of carbon

monoxide on uranium hydride (26). Uranium carbonyl has not been prepared to date.

Acetic acid vapor at 300° was found to give a brown powder, presumably a mixture of oxide and carbide (29). Hydrogen cyanide similarly produced a mixture of carbide and nitride.

When heated to 500° in a current of ethylene (13), a slow reaction took place, giving a black product containing unreacted uranium metal. Methane reacted similarly at 550°, giving uranium monocarbide, as shown by x-ray analysis.

G. The Purification of Laboratory Gases[1]

By taking advantage of the extraordinary reactivity of the hydride and the powdered uranium formed by thermally decomposing it, and of certain compounds prepared from them, a particularly simple and thorough method of purifying certain gases often used in the laboratory has been developed (39). These include the inert gases, hydrogen, deuterium, hydrogen chloride, hydrogen bromide, nitrogen, and possibly others.

The procedure for purifying the rare gases consisted of packing a vertical quartz, Vycor, or Pyrex #172 tube with cleaned uranium turnings, conversion to uranium hydride, and

---

[1] The use of uranium hydride or substances prepared from it to purify laboratory gases is due to A. S. Newton.

67-L-295

decomposition under vacuum at 500°. Glass wool filters were
packed into each end of the tube before the hydride formation.
In use, a stream of the inert gas was passed through the tube,
with the first 15 or 20 cm. of the powdered metal maintained
at 750 to 800° with a small resistance furnace. This left
30 or 40 cm. of the tube protruding beyond the furnace, caus-
ing a temperature gradient, the last few centimeters of the
uranium column being at room temperature. Impurities such
as nitrogen, oxygen, water, hydrogen, etc., were completely
removed by the metal; hydrogen alone passed through the hot
portion of the tube, but was absorbed by the cooler uranium
powder. As the heated uranium was depleted, the furnace was
moved along the tube. The tubes used were slowly etched by
the uranium at the high temperature.

The purification of hydrogen or deuterium was done in
either of two ways. A bulb charged with uranium was sealed
through a stopcock to the apparatus in use, and after con-
version of the metal to its hydride or deuteride, the hydro-
gen or deuterium was driven off by heat. This batch process
gave hydrogen free even from the rare gases. The uranium
was used over and over again. A continuous process which
freed hydrogen from all impurities except the rare gases
was identical with the one for the purification of the rare
gases, except that the column of uranium metal was heated
over its whole length; a 10 to 15 cm. length was sufficient.
The purified hydrogen did not tarnish a shiny uranium surface
at 600°.

The uranium trichloride prepared by the reaction of hydrogen chloride with uranium hydride was itself very reactive, and removed oxygen, water vapor, and chlorine from a stream of hydrogen chloride. In practice, a horizontal tube was packed with uranium, this converted to the hydride, and hydrogen chloride passed in. After complete conversion to uranium trichloride, the tube was clamped in a vertical position and its contents tamped down. Hydrogen chloride was passed through continually, and was stripped of its impurities when the uranium trichloride was heated to 400-500°. The purification of hydrogen bromide was exactly analogous, employing uranium tribromide at 350-400°.

Nitrogen is difficult to free from oxygen impurities by the classical methods. Uranium nitride was prepared by passing nitrogen over the hydride at elevated temperatures, and it was found that after all of the nitride had been formed, the ensuing nitrogen was oxygen-free. Thus the oxygen impurity reacted with uranium nitride, forming uranium oxide and nitrogen, when the reaction tube was at 500°. The purified nitrogen gave negative tests for oxygen and oxides of nitrogen. One advantage of these methods of purifying gases is that in all cases gas-solid reactions are employed, and the use of liquids is avoided.

H. Reduction of Organic Compounds

The possible use of uranium hydride as a reducing agent
for organic compounds was apparent soon after it had first been
prepared in a pure state. Experiments were conducted using
naphthalene, maleic anhydride, and nitrobenzene (40, 41).

In the case of naphthalene, the experiment was made
using the hydrocarbon with a relatively small quantity of
uranium, in the hope that in the presence of an excess of
hydrogen, the hydride would be re-formed after it had re-
duced the naphthalene. Fifty grams of naphthalene and five
grams of clean uranium turnings were heated in a high-pressure
bomb to 250°. The hydrogen pressure was maintained at 104
atmospheres, and the bomb was shaken constantly. After an
hour the bomb was cooled and opened, and it was found that
the uranium metal had been broken down to the hydride. The
melting point of the naphthalene from the bomb was identi-
cal with that of the original sample, showing that very
little if any reaction had taken place. As a matter of
fact it has already been shown (p. 11) that the reverse of
the above attempted reduction is thermodynamically favored,
namely the dehydrogenation of tetralin and decalin by
uranium to form naphthalene and uranium hydride.

The reduction of maleic anhydride to succinic anhydride
was attempted in a similar manner, but at atmospheric pressure.
The uranium used was powdered by hydride formation and

SECRET

decomposition, and the maleic anhydride dissolved in dioxane was added. Hydrogen was bubbled through the liquid as the temperature was raised to $100°$, but tests of the product showed that no significant amount of reaction had occurred. A modification was tried as follows: uranium (3.5 g.) was converted to its hydride, and maleic anhydride crystals (2.0 g.) was added. The organic substance was melted and refluxed (b.p. $200°$) for 4.5 hours, when a viscous dark brown liquid remained. Attempts to isolate crystals from both water and dioxane were fruitless. The material gave a strong unsaturation test (reaction with permanganate), despite the use of an excess of uranium hydride; apparently little or no reduction occurred.

The reduction of nitrobenzene to aniline was attempted first using an excess of uranium hydride and second using an excess of nitrobenzene. In the first trial 3.5 g. of nitrobenzene was refluxed using a salt bath at $180-185°$ with 15 g. of uranium previously converted to the hydride. After sixteen hours the resulting paste was cooled, extracted with ether, and filtered. The filtrate, which was greenish, was extracted with dilute hydrochloric acid; the aqueous phase was then made alkaline. No oily layer of aniline formed, but rather a trace of an amorphous precipitate, which could not be identified. In a second experiment with the excess of nitrobenzene (8 g.) and the same amount of uranium hydride as before, the flask was heated only three hours, the suspected amine was separated as before, cooled

SECRET

71-R-295

in acid solution to 0°, a little sodium nitrite added, and
then alkaline beta-naphthol. Only a slight pink color
formed, whereas aromatic amines usually give vividly colored
dyes when subjected to this sensitive diazotization-coupling
test. The evidence indicated that no amine was formed.

The above experiments are by no means exhaustive, and
it is probable that valuable processes could be realized by
more extensive investigations; the use of uranium deuteride
may also prove useful.

I. Uranium Triflouride: Its Preparation

and Properties

Another reaction was discovered which again demonstrated
the exceedingly high reactivity of the uranium prepared by
the decomposition of uranium hydride. Considerable interest
had been shown in uranium trifluoride, and a number of at-
tempts had been made to prepare the substance, all without
success. It was shown that although the action of hydrogen
chloride on the hydride yielded uranium trichloride, the
action of hydrogen fluoride nevertheless gave uranium tetra-
fluoride. Uranium trifluoride was prepared for the first
time, however, easily and in large quantities, by the re-
duction of uranium tetrafluoride with uranium powdered by
decomposition of the hydride (42). Since this represents
the first preparation of this substance, it will be discussed
in some detail.

1. Preparation

In the first experiment a few grams of uranium were
converted to its hydride and decomposed at 275° under vacu-
um. It was ground with the stoichiometric amount of uranium
tetrafluoride in a carbon dioxide-filled dry box, trans-
ferred to a nickel boat, and heated in a quartz tube to 1000°
in a stream of argon. After cooling, the material was tested
by heating from room temperature to 250° in an atmosphere
of hydrogen, and it was found that no absorption occurred,
indicating the absence of unreacted uranium metal. The
black mass was subjected to x-ray analysis, and a new set
of diffraction lines were found, showing the presence of a
new phase. Thus it was seen that uranium trifluoride had
been formed according to the equation:

$$U + 3\ UF_4 \longrightarrow 4\ UF_3$$

The preparation was repeated on a larger scale by mix-
ing 101 g. of cleaned uranium turnings with 400 g. of pure
uranium tetrafluoride in a large nickel tube holding a
delivery tube leading to the bottom. The system was flushed
with hydrogen and heated to 250° until no more hydrogen
was absorbed, and the uranium hydride-uranium tetrafluo-
ride mixture was cooled and mixed thoroughly by shaking.
The tube was heated while a slow stream of argon passed
through until the temperature was 1100°, which was main-
tained for two hours. On cooling a black, dense, coke-
like product was observed.

Analysis of the uranium trifluoride by the pyrohydrolytic method (42) gave the following results:

	Calculated for UF_3	Found
U	80.7%	80.2%
F	19.3	19.2

The analysis corresponds to a fluorine-uranium ratio of 3.005.

2. Physical Properties

The density of uranium trifluoride, measured with a helium densitometer (22), was 8.1 ± 0.1 g./cc. The crystal structure, as revealed by x-ray diffraction studies, was hexagonal, with $a = 4.13 \pm 0.01$ A and $c = 7.33 \pm 0.01$ A, with two UF_3 molecules per unit cell. An attempt to determine the melting point by heating a sample in a graphite crucible surrounded by helium in an induction furnace gave evidence that the material decomposed. A heating curve gave a break at $1610^{\circ} \pm 20^{\circ}$; inspection of the crucible showed a sublimate of fine blue-green crystals in the upper part, which by analysis were shown to be impure uranium tetrafluoride. The residue was a black button containing 90 per cent uranium, and was presumably uranium dicarbide. The evidence thus suggested disproportionation with subsequent reaction of the uranium with crucible:

$$4 \; UF_3 \longrightarrow 3 \; UF_4 + U$$
$$U + 2 \; C \longrightarrow UC_2$$
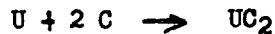
3. Chemical Properties

A few chemical reactions of uranium trifluoride were examined. When boiled with hydrochloric acid, a green precipitate formed in a green solution, with a little evolution of a gas. This suggested the following reaction:

$$4\ UF_3 + 4\ HCl \longrightarrow 3\ UF_4 + UCl_4 + 2\ H_2$$
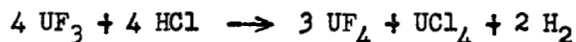
A mixture of hydrochloric and boric acids rapidly dissolved uranium trifluoride. Silver perchlorate was quickly reduced to the metal. Chlorine, bromine, and iodine each reacted, forming the corresponding uranium monohalotrifluoride (36).

J. The Classification of Uranium Hydride

According to Emeleus and Anderson (44), the compounds of the elements with hydrogen fall into three fairly distinct classes, namely: the volatile hydrides, the salt-like hydrides, and thirdly a group of substances derived from metals in which the proportion of hydrogen varies with temperature and pressure. The last may be considered interstitial compounds. An example of the first type is water or stibine, of the second type sodium or calcium hydride, and of the third class the palladium-hydrogen system. Data on the rare earth metal hydrides are inaccurate and contradictory, but they belong to the salt-like or interstitial type, or to yet another type.

It is interesting to consider uranium hydride in re-
lation to the above classification. The foregoing studies
lead to the belief that uranium hydride is of the salt-like
type. The evidence for this classification is summarized
below:

1. The composition of uranium hydride, after
taking into account the effect of the various im-
purities, showed that the hydrogen-uranium ratio
was a whole number, namely three, rather than a
fractional value which is characteristic of the
interstitial hydrides.

2. The constancy of composition of the uranium
hydride prepared over considerable temperature and
pressure ranges indicated the formation of a definite
compound.

3. The pressure-composition isotherms were
characteristic of a salt-like hydride, except for the
unexplained dip near 97 mol per cent hydride.

4. The linearity of the density-composition curve
showed that the system was not an imperfect solution,
as may be expected of an interstitial system.

5. The failure of hydrogen to transfer from the
hydride to the metal isothermally indicated the
absence of solid solution phenomena, and of two differ-
ent hydrides.

6. The x-ray diffraction studies indicated compound formation rather than solid solution or interstitial compound formation.

VII. URANIUM HYDRIDE AMALGAM AND RELATED MATERIALS

A. Formation and Physical Properties of Uranium Hydride Amalgams

1. Formation, Properties, and Recommended Procedure for Preparation

In some experiments with a uranium-gold alloy, a sample was treated with hydrogen at 250° until a powder resulted, and an attempt was made to separate any elementary gold by amalgamation (45). It was observed that the entire mass was "wetted" by the mercury, and appeared to dissolve. A series of hydride samples prepared from pure uranium was then treated with mercury, forming "amalgams" of increasing hydride concentration (13). The preparations were extremely bright and shiny, and some had a marked tendency to adhere to the glass walls of the vessel. The amalgams failed to adhere to any greasy spots inside the glass containers. It was found that hydride samples which had been briefly exposed to the air prior to the mercury treatment were not wetted and did not amalgamate. Close examination of a

shiny hydride amalgam preparation revealed the presence of

a few unaffected particles; these were probably the im-

purities present in the original metal.

The consistency and appearance of uranium hydride

amalgams as a function of concentration are indicated in

Table 2 (45, 46).

Table 2. Variation of the Appearance of Uranium Hydride
Amalgams with Concentration

Concentration	Description
10% UH_3	Much like mercury itself; scarcely adheres to glass
20	Definitely more viscous; adheres to glass; has appearance of gallium metal
30	Semi-fluid mass; adheres to glass readily
40	Semi-solid; hardly flows; adheres to glass
50	Stiff semi-solid; does not flow; adheres to glass
60	Borderline between solid and semi-solid; adheres to glass in spots
70	Light gray metallic looking powder; does not adhere to glass
80	A gray powder; pyrophoric
90	A dark gray powder; pyrophoric

When uranium hydride amalgams were prepared, no heat

was given off. This is in contrast to the process of

forming amalgams of uranium metal, powdered by formation
and decomposition of the hydride; a small but definite
amount of heat is liberated as uranium-mercury interme-
tallic compounds are formed (47).

Uranium deuteride was found to form amalgams indis-
tinguishable in appearance from hydride amalgams.

Recommended Procedure for the Preparation of
Uranium Hydride Amalgams. A simple apparatus such as
that shown in Fig. 8 is constructed, and the flask
charged with a known amount of cleaned uranium turn-
ings. The desired amount of mercury is poured into
the side-arm reservoir, and the whole apparatus flushed
thoroughly with hydrogen purified over powdered urani-
um. The flask is lowered into a molten salt bath and
heated to 250°. After complete conversion to uranium
hydride, the flask is removed from the bath, cooled,
washed, and dried. The inlet and outlet stopcocks
are closed, leaving the apparatus full of hydrogen,
or, alternatively, the apparatus is evacuated before
closing the stopcocks. The mercury reservoir is
rotated in its ground glass joint, permitting the
mercury to flow down onto the hydride.

Many modifications of the apparatus and pro-
cedure above may be made. The mercury may be stored
in a separate funnel and permitted to run in by opening
a stopcock, or may be held in a side arm until needed,
when the whole apparatus is tipped. Substances other
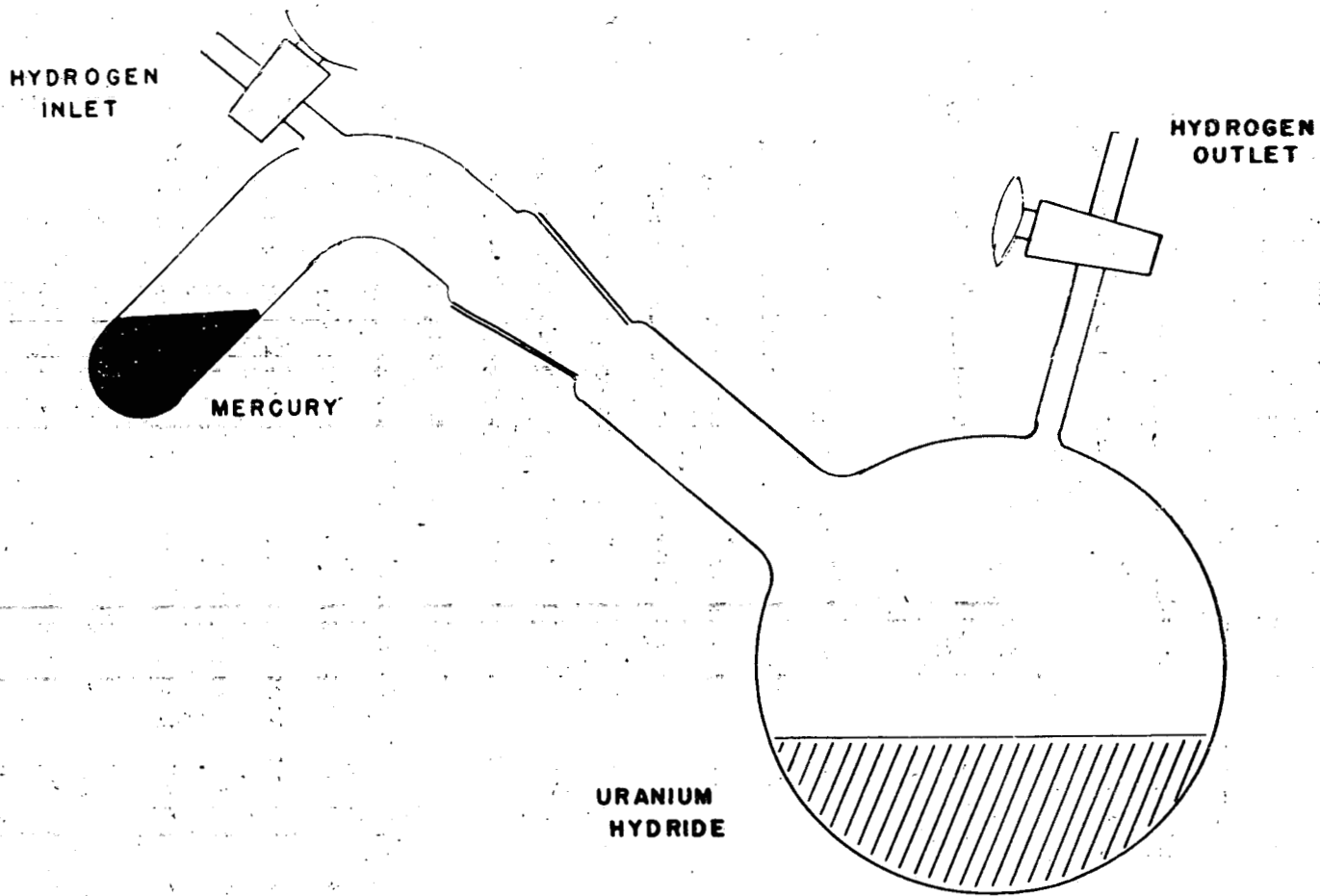
HYDROGEN INLET

HYDROGEN OUTLET

MERCURY

URANIUM HYDRIDE

FIG. 8 APPARATUS FOR PREPARATION OF URANIUM HYDRIDE AMALGAMS

than mercury (as in experiments on the chemical proper-

ties of the hydride amalgam) may be introduced by the

rotating ground glass joint technique. Thickened con-

strictions for sealing off under vacuum may be built

in. Well-fitting rubber stopper connections are

satisfactory if no great time elapses after preparation

of the hydride.

2. The Radiochemical Properties and Nature of Uranium Hydride Amalgams

The formation and the uncommon and unexpected character

of uranium hydride amalgams gave rise to speculations on the

disposition of the hydride in the mercury. Samples of the

semi-liquid amalgams were filtered centrifugally through

porous alundum disks (45). It was found that the filtrate

contained less than 0.1 per cent hydride, while the residue

was a more concentrated, nearly solid amalgam. In experi-

ments in which some hydride amalgams were being compressed

in steel dies at high pressures (46), mercury almost free

of uranium was extruded from the crevices; the uranium

hydride concentration was raised from 60 to 67 per cent.

The radiochemical studies discussed previously (p. 32)

were extended to hydride amalgams prepared from bombarded

uranium containing radioactive xenon. An apparatus con-

sisting of a flask with a sealed-off side arm containing

mercury, connections for introducing hydrogen, and a

counter attached through a stopcock, was charged with the
bombarded uranium. After conversion to uranium hydride, in
which process less than one per cent of the radio-xenon es-
caped, the apparatus was tipped so that the mercury flowed
onto the hydride, forming the amalgam. Again not more than
one per cent of the xenon was released, as shown by the
counter. Even when the amalgam was boiled, very little more
of the xenon was liberated. It was found that in order to
effect quantitative release of the radio-xenon, the uranium
hydride had to be dissolved completely in such reagents as
silver perchlorate solution.

It was necessary to conclude from the above experiments
that uranium hydride amalgams are not true solutions, but
that they are suspensions of the hydride particles in
mercury. The amalgams are in all probability colloidal dis-
persions in which each particle retains its own structure.
No previous examples of such a hydride amalgam are known.

B. Chemical Properties of Uranium Hydride Amalgams

1. Action of Air

a. Coagulation of the hydride amalgams by exposure to
air. When a liquid uranium hydride amalgam was exposed to
the air, a dark brown powdery substance began to appear on
the surface in a most remarkable manner; small brown spots
appeared which grew until the whole mass was covered. In

some investigations of the reaction and of the brown product
(46), 270 g. of 20 per cent uranium hydride amalgam was pre-
pared and air was bubbled through it for 12 hours, when a
large amount of brown precipitate had formed. The mixture
was exposed to air for 48 more hours. Enough heat was
evolved by the aeration to maintain the temperature of the
entire mass 6° above room temperature for several hours
from the time the aeration began. The bulk of the mercury
was then separated by pouring through a paper cone with a
pin hole in its apex. Although the mercury came through
shiny it rapidly tarnished, and yielded 15 to 20 g. more
of the powder on further exposure to the air.

The brown powder was intimately mixed with mercury.
It was analyzed in the same fashion that uranium hydride was
(p. 13), 7 to 10 g. samples being used. The combustion in
oxygen was sometimes violent. The mercury contained in the
sample condensed in the cooler end of the combustion tube.
It was dissolved out with nitric acid at the end of the
analysis and titrated with standard potassium thiocyanate
solution, using ferric alum as the indicator, according to
the method of Low (48). The weight of mercury thus found
was subtracted from the weight of the sample taken, permit-
ting the calculations of the analysis of the brown powder
on a mercury-free basis. The following results were

obtained:

	U	H	H/U ratio
Trial 1	97.44%	1.17%	2.85
Trial 2	97.47	1.16	2.82

These showed that the brown powder was still mostly uranium
hydride, probably mixed with uranium dioxide, which is brown.
That the brown powder was principally uranium hydride was
confirmed by other evidence. Its x-ray diffraction pattern
was identical with that of the ordinary hydride. Samples
on several occasions caught fire spontaneously, reacted with
nitric acid, with hydrochloric acid-hydrogen peroxide mixtures,
and with silver perchlorate solution in the same way uranium
hydride did. Another sample was heated in a vacuum, dis-
tilling off the mercury, and decomposing the hydride to free
uranium. This readily took up hydrogen again, and the
hydride thus formed again formed an amalgam, but a consider-
able amount of scum was left unaffected by the mercury; this
was presumably uranium oxide.

Some difficulty was encountered in separating the fine
droplets of mercury from the brown powder. A fairly satis-
factory way was devised, which consisted of suspending the
powder in petroleum ether, which left most of the mercury
towards the bottom of the containing vessel, and decanting
quickly into another vessel (49). This operation was
repeated several times, which gave a product quite low in

84-2-295

mercury. A petroleum ether suspension of this material was filtered using a sintered glass crucible with suction; the wetted powder formed a mat against the fritted-glass bottom, while the mercury had a tendency to collect together in a drop, which could be removed. In this fashion several grams of product was produced which gave a negative test for mercury.

An interesting observation was made incidental to the work described above: Some 25 per cent uranium hydride amalgam, left over from a previous experiment, was frozen in an impression in a lump of solid carbon dioxide. After freezing solid, the surface was scraped clean; the shiny appearance was not changed by tarnishing, even overnight, except for the condensation of atmospheric moisture (50). When the frozen pellet was removed and allowed to melt, the characteristic formation of the brown powder took place as usual.

   b. Rate of coagulation of uranium hydride amalgams by exposure to air. In order to learn more about the process by which air causes uranium hydride to separate from its amalgams, two amalgams were prepared in wide mouth flasks, and exposed to air for periodic weighings (46). The first preparation was 106 g. of a 28.7 per cent hydride amalgam, and the second was 111 g. of a 30.8 per cent amalgam. After exposure to the air the samples were weighed frequently at

the beginning, and then less and less frequently. The weight
gains were followed for three years, and are given in Table 3.
The brown powder gradually darkened, finally becoming black.
The data for the first sample in Table 3 are plotted in Fig. 9.
This shows that the most rapid absorption of oxygen occurred
at the beginning; the rate dropped in the case of the first
sample from an initial value of about 1 mg. of oxygen per
minute to about 1.7 mg. per day near the end of the time of
observation. The gain in weight was most probably attributa-
ble to two processes: the action of oxygen which precipi-
tated the hydride from the amalgam, and the subsequent slow
oxidation of the hydride on standing in air. After standing
for 1092 days, the weight gain of one sample was 74.5 per
cent of that expected for conversion of all of the uranium
to U_3O_8.

    c. Rate of formation of water by the aeration of uranium
hydride amalgam. It was shown earlier that the hydrogen to
uranium ratio of the hydride precipitated from amalgams was
lower than in the pure hydride, i. e., about 2.83 rather
than 2.97. It was shown above that the rate of gain of
oxygen was initially rapid, and then tapered off. When the
H/U ratio dropped to 2.83 after the hydride was precipitated
from mercury by air, the most probable fate of the hydrogen
lost was the formation of water, and it was interesting to
determine the rate with which water was formed, and compare
it with the rate of weight gain.

Table 3. Weight Gain of Uranium Hydride Amalgams
on Exposure to Air

Sample No. 1		Sample No. 2	
Total time elapsed (days)	Gain (mg.)	Total time elapsed (days)	Gain (mg.)
0.0	0.0	0.0	0.0
.0035	4.6	.0035	24.8
.007	8.2	.021	56.5
.13	87.0	.15	152
.19	120	.25	194
.67	212	.71	260
.97	231	1.00	277
1.66	253	1.67	298
2.62	275	2.25	315
4.59	310	3.63	347
5.62	326	4.67	366
6.67	341	5.71	384
7.15	352	6.70	399
8.63	365	7.70	414
9.67	381	8.71	432
10.9	397	9.90	451
11.8	406	10.9	463
13.9	430	12.0	480
15.1	443	13.0	490
16.6	460	14.1	506
17.9	475	15.7	525
19.1	489	17.0	541
20.6	506	18.2	559
22.7	520	19.7	578
25.6	546	21.8	594
27.7	564	26.7	645
32.0	595	31.0	681
37.8	642	36.9	736
46.5	704	45.6	808
53.8	751	52.8	861
83.0	912	81.8	1042
200	2102	199	2381
590	3127	589	3526
1092	4006	1091	4533
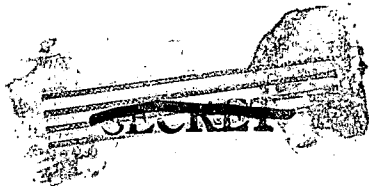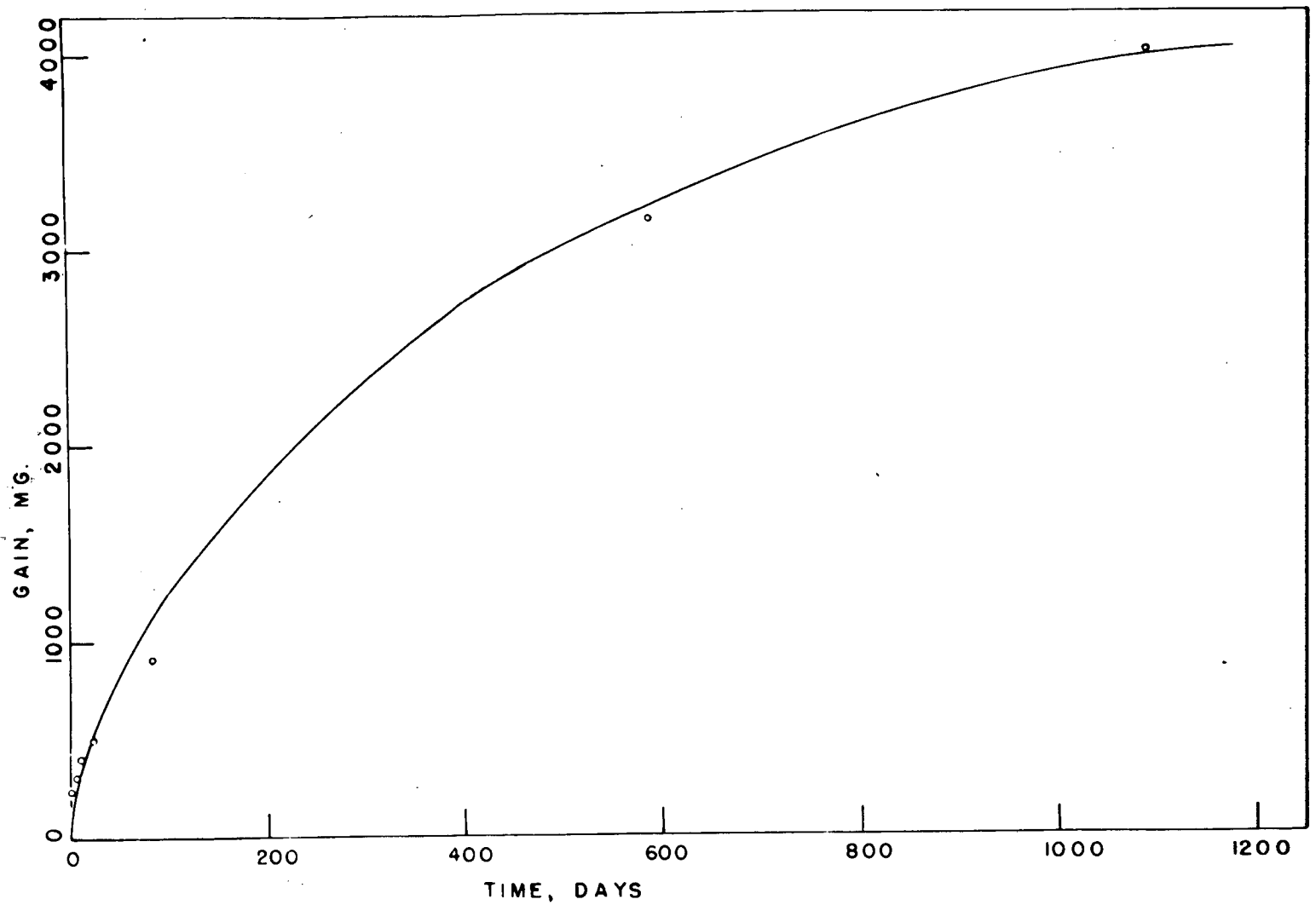
87-ℓ-295

FIG. 9   WEIGHT GAIN OF UH₃ AMALGAM ON AERATION
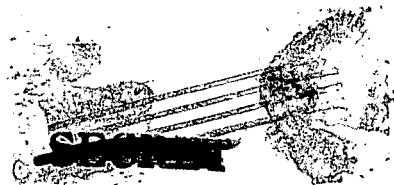
One hundred and thirty-four grams of 21.6 per cent

uranium hydride amalgam was prepared in a flask equipped

with a delivery tube leading under the surface of the mercu-

ry (50). A slow stream of air, dried by anhydrous magnesium

perchlorate, was bubbled through the liquid, and was then

filtered through a tube containing fine glass wool to remove

suspended particles of the solids. The stream was then

passed through a small tared weighing tube packed with an-

hydrous magnesium perchlorate, which was weighed periodically.

Table 4 below shows the amount of water formed over a three-

month period.

Table 4. Formation of Water by the Aeration of
Uranium Hydride Amalgam

Time elapsed (days)	Water formed (mg.)
0	0.0
2	14.3
7	29.0
14	46.9
23	58.2
33	67.0
55	82.0
84	97.1

The data in Table 4 are plotted in Fig. 10, and it is

seen that the water is formed most rapidly at the beginning,

the curve having the same general shape as that in Fig. 9.
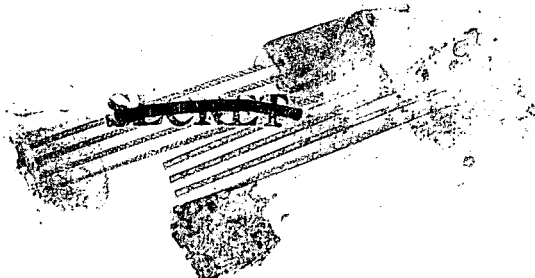
FIG. 10 FORMATION OF WATER BY AERATION OF UH_3 AMALGAM

d. **The aeration of uranium amalgams.** It is of interest
here to briefly present the results of some experiments on
the aeration of uranium amalgams, as contrasted to the uranium
hydride amalgams. The uranium amalgams were prepared by ad-
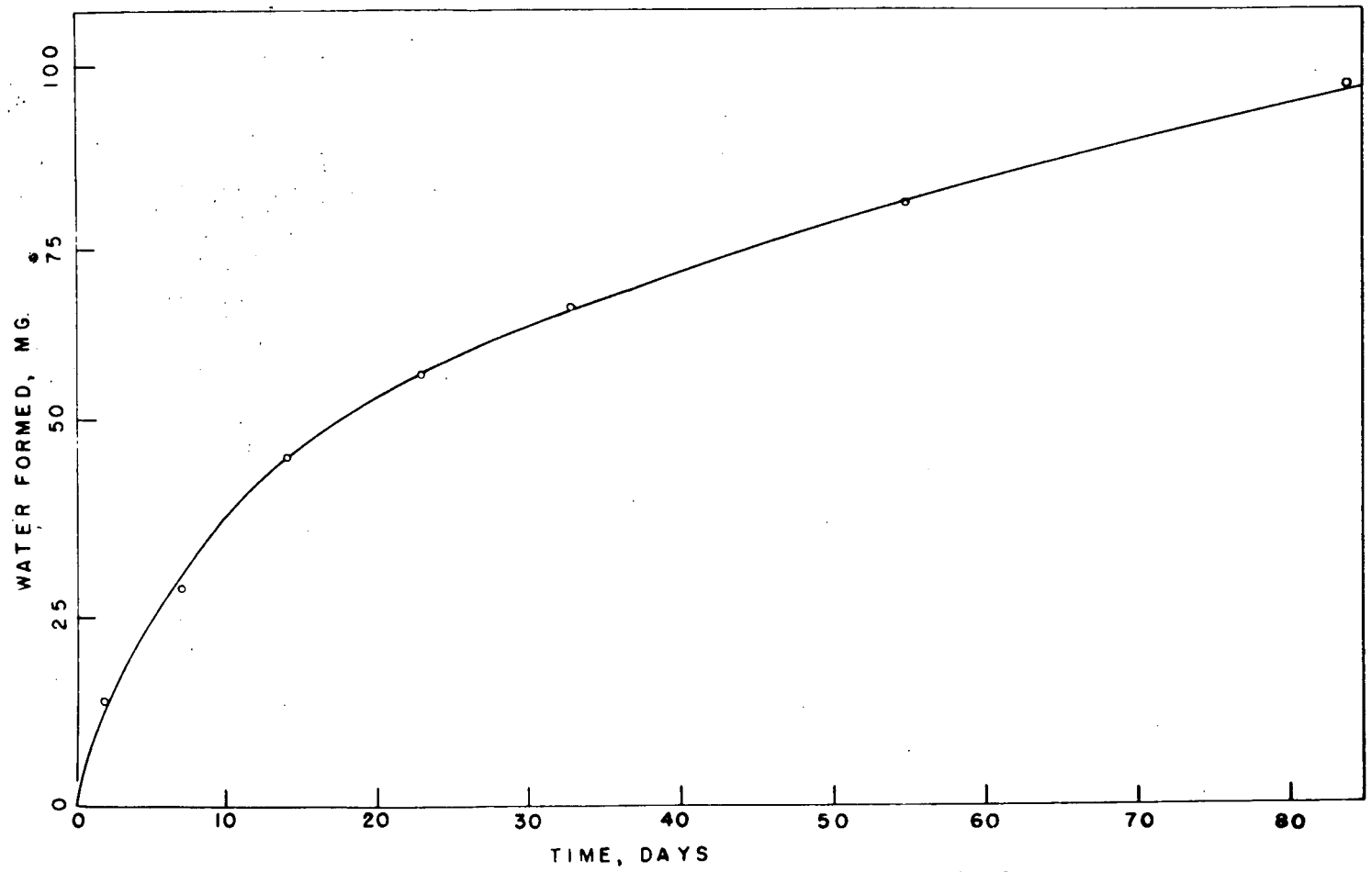dition of mercury to finely divided uranium formed by decom-
posing the hydride (45). Some heat was given off, indicating
that intermetallic compounds were being formed. It was found
that on exposure to air a rather rapid increase in weight
took place as a dark solid separated (52). If the weight gain
had corresponded to the oxidation of the uranium to U_3O_8, a
gain of 15.2 per cent would be expected, based on the uranium
alone; actually one sample gained 19.9 per cent, another
22.0 per cent, within a two-month period. This strongly sug-
gested that oxidation of the U-Hg intermetallic compounds
gave oxides of both elements rather than of uranium alone.
Support of this conclusion was gained when an oxidized sample
was leached with dilute hydrochloric acid, which dissolves
HgO but not U_3O_8; the leachings gave a strong test for mercury.

2. Action of Water Vapor

It had been observed that a precipitate formed when
uranium hydride amalgams were treated with water vapor. This
reaction was studied by amalgamating the hydride prepared
from 10 g. of uranium with 70 g. of mercury in a small flask,
and passing purified hydrogen, saturated with water vapor,
through the apparatus for a month (53). The flask and its

contents were weighed periodically. A grayish-brown en-

crustation slowly formed over the surface of the amalgam.

The weight gain was about 15 mg. per day at the beginning,

gradually dropping, until after 10 days it was about 5 mg.

per day. After a month the hydrogen stream was shut off

and a little water poured into the flask, which was allowed

to stand another month. A slight pressure was built up

during this time, which was relieved by occasionally open-

ing the stopcock.

The water was decanted off, and the powder was sepa-

rated, washed with alcohol and ether, and dried. A sepa-

ration from the small droplets of mercury was made by the

petroleum ether suspension technique already described (p. 71).

The dried brown powder freed from mercury burned readily

when ignited. Analysis of the material for uranium by ig-

nition to U_3O_8 disclosed that it contained 96.6 per cent

uranium, which shows that it was mostly uranium hydride,

presumably contaminated with a uranium oxide.

3. Action of Hydrogen Sulfide

Some 25 per cent uranium hydride amalgam was prepared

in a flask, and a slow stream of hydrogen sulfide passed

through (50). When the hydrogen sulfide was first passed

in, a fine black powder separated immediately. After 36

hours several grams of a black material had separated. The

contents of the flask were emptied in a carbon dioxide-filled

dry box, and the black powder separated from the bulk of the mercury. The droplets of mercury were separated by the petroleum ether flotation technique.

The dried mercury-free powder thus prepared was analyzed by combustion in the apparatus previously employed in the analysis of uranium hydride (Fig. 2). A modification was introduced in order to determine the sulfur content. This consisted of a small length of tubing holding several coiled strips of platinum inserted after the combustion tube, heated to about 500°. This caused the catalytic oxidation of sulfur dioxide to the trioxide. The mixture of water and sulfur trioxide thus formed was caught in a small weighing tube containing both sodium hydroxide and anhydrous magnesium perchlorate. Thus weighing this tube gave the total of water and sulfur trioxide. The contents of the tube were then dissolved in water and barium chloride added; the barium sulfate formed was filtered off, ignited, and weighed.

In this fashion two analyses were run, giving H = 1.01, 0.92 per cent, and S = 0.62, 0.65 per cent. The samples continously evolved traces of hydrogen sulfide, probably because of hydrolysis of uranium sulfide present by atmospheric moisture.

It thus appeared that the action of hydrogen sulfide, like water, also caused uranium hydride to separate from its mercury suspension. In this case the hydride thus separated probably continued to react slowly with the hydrogen sulfide,

giving some uranium sulfide. It is probable that the action

of air, water, and hydrogen sulfide are all similar in that

they react with the surface of the hydride particles in the

mercury suspension, which is likely a colloidal suspension,

and cause the separation of a product which is predominately

uranium hydride.

4. Hydrogen-Deuterium Exchange in Uranium Hydride and Deuteride Amalgams[1]

In connection with the attempts to separate deuterium

from hydrogen employing uranium hydride or its amalgam, ex-

periments were run in which the rates of exchange of hydrogen

with uranium deuteride amalgam and deuterium with uranium

hydride amalgam were measured (6). In the first experiment

a 25 per cent uranium deuteride amalgam in a flask containing

hydrogen at about 400 mm. pressure was heated to $350°$. Samples

of the gas were removed periodically and analyzed by the gas

density balance. It was found that after 5 minutes the hydro-

gen contained 0.2 per cent deuterium, after 15 minutes 2.7

per cent, and after 2 hours 10.3 per cent. This amount of

deuterium could be accounted for by the thermal decomposition

of the deuteride at $350°$. The second experiment was similar

except that uranium hydride was prepared, and the atmospheric

gas was deuterium. Comparable results were obtained. It may

---

[1]This Section is based on the work of O. Johnson and R. W. Nottorf.

be concluded that no exchange took place, and that when the
hydride or deuteride in mercury suspension decomposed, the
uranium thus released reacted with the mercury forming an
intermetallic compound, which does not react with hydrogen.
It will be recalled that with uranium hydride itself at 300°,
complete and rapid exchange with deuterium was observed.

5. Reduction of an Organic Compound with Uranium Hydride Amalgam

It was shown earlier (p. 57) that although some organic
compounds could be reduced with uranium hydride, the reactions
were unsuccessful from the standpoint of yielding the expected
products. In order to determine whether the hydride amalgam
would be a more satisfactory reducing agent, an experiment
was conducted with maleic anhydride (41). Ten grams of
uranium was converted to the hydride in a flask with a long
sealed off side arm holding 1.8 g. of maleic anhydride. The
flask was equipped with a vertical tube which acted as an
air condenser, and at the top was a dropping funnel holding
30 g. of mercury, which was run in, forming the amalgam.
The apparatus was tipped so that the maleic anhydride could
be tapped in, and the flask was heated in a salt bath until
the organic compound began to reflux. After 15 minutes the
apparatus was cooled and washed out with dioxane. After
filtering, the solvent was evaporated. A thick brown syrup

remained, very similar to the one prepared from the uranium

hydride reduction itself. No crystals could be obtained.

C. Related Materials

It was of interest to determine whether mercury was unique

in its ability to wet uranium hydride, or whether other liquid

metals also had this property (46, 54). Sodium forms alloys

with potassium which are liquid at room temperature; 20 ml.

of such an alloy, containing 40 per cent sodium, was allowed

to run upon two grams of uranium hydride in an apparatus simi-

lar to that employed in the preparation of hydride amalgams.

The sodium-potassium alloy appeared to wet the uranium hydride,

forming a composition of the same general appearance as the

amalgams.

Wood's metal and tin were also tested in a similar fashion

(46). A flask containing 5.2 g. of uranium was heated to

250° with hydrogen passing through it, until complete con-

version to the hydride had occurred. After cooling a lump

of Wood's metal (an alloy of bismuth, lead, tin and cadmium,

m. p. 60.5°) weighing 16.8 g. was lowered on to the hydride.

The flask was heated until the alloy melted. After a few

minutes shaking, the alloy began to expand rapidly, forming a

spongy mass which completely filled the flask (about 40 ml.).

It is probable that the liquid alloy wetted the uranium hydride,

and reacted with it, forming intermetallic compounds of uranium

with the constituents of the Wood's metal. This process
would liberate hydrogen in the interior of the mass, forming
a froth of the still liquid metal. The experiment was re-
peated using tin (m. p. 232°) in place of the Wood's metal.
With the hydride prepared from 6.1 g. of uranium, 11.7 g. of
tin at 240° also expanded rapidly to a spongy mass whose
volume was about 12 ml.

In order to determine whether mercury would "amalgamate"
hydrides other than uranium hydride, an experiment was con-
ducted with the mixed rare earth hydrides prepared by heating
"Mischmetall" in hydrogen (55). The rare earth metal mixture,
principally cerium and lanthanum, was quite impure, and did
not disintegrate when heated in hydrogen. Mercury appeared
to have but little action on the product, but when some of
the mercury was poured out into the air, a fragile, ash-like
yellow encrustation slowly formed on the surface. The evi-
dence was insufficient to distinguish between rare earth
metal amalgam and a rare earth hydride amalgam. It would be
interesting to investigate these phenomena more fully.

VIII. USES OF URANIUM HYDRIDE AND THE HYDRIDE REACTION

As stated in the introduction, there were several spe-
cific reasons for investigating uranium hydride aside from
the general scientific interest, and some of the predicted

applications proved fruitful. During the course of three
year's work with this compound a number of other uses were
found and developed. These are summarized below.

A. Laboratory Source of Pure Hydrogen and Deuterium

Uranium hydride or deuteride affords a convenient labo-
ratory reservoir for hydrogen or deuterium. The hydride or
deuteride is prepared at 250° in a flask, and when needed,
the temperature is raised to whatever value gives the de-
sired gas pressure. A temperature of 430° is required to
give a hydrogen pressure 760 mm. The hydrogen or deuterium
thus evolved is free of all impurities, including the rare
gases. The only precaution necessary is to insert glass
wool filters in the lines to prevent mechanical carrying of
the fine hydride particles by the gas stream.

B. Preparation of Powdered Uranium

Powdered uranium is easily prepared by the thermal de-
composition of uranium hydride. The decomposition tempera-
ture determines the nature of the metal formed. That made
by decomposition at 450-500° is hard, and must be ground
using a mortar and pestle in an inert atmosphere. Higher
temperature cause the metal to sinter more; a shiny massive
lump is formed when heated to 900°. The recommended technique

98-1-295

is to decompose the hydride under vacuum at 250-300°, although

the dissociation pressure at this temperature is not great and

the decomposition is somewhat slow (p. 16). Metal thus pre-

pared is dark, almost black, and exceedingly reactive. Its

use as a "getter" or "scavenger" in vacuum tube work is sug-

gested. Powdered uranium may also be used in the preparation

of certain uranium alloys or compounds; for example, uranium

monocarbide, UC, is formed by heating the metal with the proper

amount of powdered carbon (56). It is usually more convenient

to mix the hydride itself with the other reaction substance

before decomposition to uranium metal. This was done in the

preparation of uranium trifluoride (p. 59). Still another

use of finely divided uranium metal is the purification of

hydrogen and the rare gases (p. 54).

C. Preparation of Uranium Compounds

1. Wet Methods

Two reactions of uranium hydride with solutions of oxi-

dizing agents serve to prepare uranyl salts: the reaction

with a mixture of hydrogen peroxide and an acid (p. 38), and

with a silver salt and silver oxide (p. 44).

2. Dry Methods

Many preparations of anhydrous binary uranium compounds

are possible by reaction with gases (p. 45 ff.). These include

uranium tetrafluoride, chlorides, bromides, iodides, oxide,

sulfide, nitride, and phosphide. The use of these compounds,

directly prepared from uranium hydride, in the purification

of laboratory gases has been discussed (p. 54).

D. Isolation of Intermetallic Compounds

As uranium hydride is in an extreme state of subdivision

and as intermetallic compounds of uranium do not react with

hydrogen, crystals of the compound can be separated by siev-

ing through a fine screen. When uranium alloys with tin,

with bismuth, and with aluminum are powdered by treating

with hydrogen at 250°, the intermetallic compounds can be

separated on a 400 mesh screen (57). An inert gas atmos-

phere must be employed. The same technique may be employed

to separate inclusions of impurities such as uranium mono-

carbide from uranium. A modified procedure takes advantage

of the slow rate of solution of uranium hydride in non-oxi-

dizing acids; thus when a uranium-tin alloy is powdered by

conversion to hydride, the tin compound reacts preferentially

with dilute hydrochloric or sulfuric acid, and may be leached

out (58).

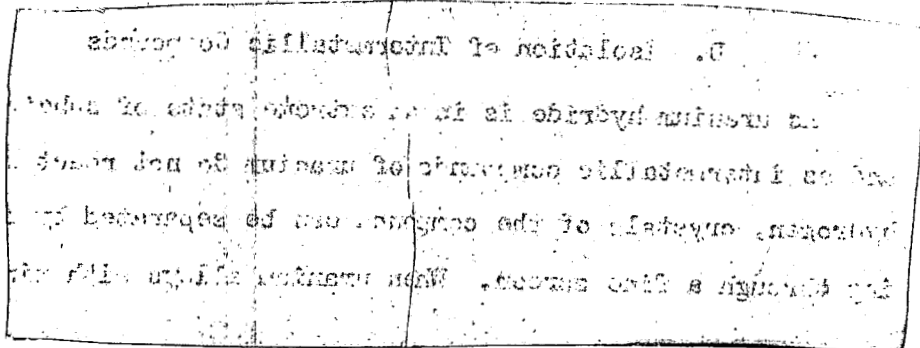## E. Etching of Metallographic Specimens

Uranium alloys containing a matrix of uranium metal may

be etched by a short treatment with hydrogen at 250° (59).

The crystals of the compound are not affected, and after re-
moval of the hydride, they are plainly visible under the micro-
scope.

G. Maintaining a Given Hydrogen or Deuterium Pressure

It is evident from the temperature-dissociation pressure
studies of uranium hydride that any desired hydrogen pressure
can be maintained in an apparatus by merely having a flask
containing a uranium-uranium hydride mixture at the proper
temperature connected to the system. Deuterium and uranium
deuteride would behave similarly. Gases other than hydrogen
in the system which react with uranium or its hydride at the
temperature involved, could not be tolerated.

H. Analysis of Metallic Uranium for the Free Element

A method for analyzing uranium samples for the free ele-
ment based on the hydride reaction has been developed (61).

A weighed sample is converted to the hydride, which is then thermally decomposed under vacuum, the volume of hydrogen evolved being measured. Few interferences are encountered, since other metals which absorb and release hydrogen as uranium does (palladium, platinum, thorium, rare earths) are rarely present in materials to be analyzed for free uranium.

I. Other Applications

The attempted use of the hydride reaction in the separation of the isotopes of hydrogen, although unsuccessful to date, may with additional modifications yield profitable amounts of deuterium. A temperature-measuring device, consisting of a hydrogen-filled bulb containing uranium, may be constructed; the pressure of the hydrogen would give a measurement of the temperature of the bulb. The slowness with which equilibrium is reached and the availability of other temperature-measuring instruments will probably prevent its use. Finally, the dehydrogenation of organic compounds with uranium and the reduction of organic compounds with uranium hydride are applications which further research may prove to be effective.

IX. SOURCE AND PURIFICATION OF REAGENTS, AND

ANALYSIS OF PRODUCTS

A. Source and Purification of Reagents

The common reagents used—acids, salts, mercury, etc.—were of Analytical Reagent quality obtainable on the market and were employed without further purification. The various organic solvents and compounds used were purchased from the Eastman Kodak Company, Rochester, New York, and were of the highest purity sold.

The uranium metal from which the hydride was prepared was manufactured by the Project, as explained in the Introduction. Analyses are given in Table 1 (p. 17). The uranium tetrafluoride employed in the preparation of uranium trifluoride was also from Project sources. Pyrohydrolytic analysis (43) gave the following results:

	Calculated for UF_4	Found
U	75.8%	75.7%
F	24.2	24.0

The water content was found to be less than 0.1 per cent (62), and the uranyl fluoride content approximately 0.4 per cent (63). The deuterium used was prepared from heavy water, also obtained from Project sources, by passing the vapor over hot uranium turnings (p. 18). It was over 99.9 per cent pure.

When ever possible commercial sources of compressed or
liquefied gases were employed. This applied to hydrogen,
argon, helium, oxygen, nitrogen, ammonia, carbon dioxide,
hydrogen fluoride, hydrogen chloride, chlorine, hydrogen
sulfide, methane, and ethylene. The purification of hydro-
gen (p. 54) and the inert gases (p. 54) has already been
described. Nitrogen and hydrogen chloride were purified
by passage over uranium nitride (p. 55) and trichloride
(p. 56) respectively. The remainder were used without puri-
fication. The hydrogen bromide was prepared by direct union
by the method of Ruhoff, Burnett, and Reid (64). Carbonyl
chloride was prepared by the action of fuming sulfuric acid
on carbon tetrachloride (65) and was scrubbed with concen-
trated sulfuric acid. Carbon monoxide was generated by the
dehydration of formic acid with concentrated sulfuric acid,
and was washed with sulfuric acid. Phosphine was produced
by the reaction between yellow phosphorus and potassium
hydroxide; it was dried by passage through a dry ice trap.
Bromine was purified by shaking with concentrated sulfuric
acid in a separatory funnel, with subsequent distillation
over phosphorus pentoxide.

B. Analytical Methods for Products

In some cases analyses were not necessary to determine
the composition of products formed, since a given weight of

uranium was used, and the total weight of the product could be determined, which gave the composition at once.

Uranium analyses were made either titrimetrically or gravimetrically, depending upon convenience. In the titrimetric determinations the compound was converted into a uranyl solution, reduced in an amalgamated zinc-filled Jones reductor, aerated to re-oxidize the small portion of trivalent uranium formed, and titrated with standard ceric sulfate using ferrous-1, 10- phenanthroline sulfate as the indicator (66). The gravimetric determinations were made by either igniting the uranium compound directly to U_3O_8, or precipitating ammonium diuranate from solution, and igniting it to U_3O_8 (66).

The analysis of uranium hydride has already been discussed (p. 13 ff.). Mixtures of hydrogen and deuterium were analyzed by the gas density balance of Stock and Ritter (24).

The uranous acetate was analyzed for tetravalent uranium by direct titration. The acetate content was determined by distillation with phosphoric acid and titrating the acetic acid in the distillate.

Uranium trifluoride was analyzed by pyrohydrolysis (43). Uranium chlorides and bromides were analyzed by dissolving in water, oxidation of the uranium to the hexavalent state with hydrogen peroxide, and precipitation of the halide with silver nitrate (67).

SECRET

X. CONCLUSIONS AND SUMMARY

1. Pure uranium metal reacts rapidly with hydrogen at 250°C, yielding a fine, black, pyrophoric powder, uranium hydride. Analysis shows a composition corresponding to the formula $UH_{2.97}$, but when the effects of impurities in the metal are taken into account, the formula of the compound formed is shown to be UH_3.

2. Deuterium reacts with uranium analogously, forming uranium deuteride. UD_3.

3. Uranium hydride UH_3 is also formed by the action of steam, or of certain organic compounds, such as tetralin, on uranium U.

4. The physical and thermodynamic properties, x-ray analysis, and the chemical composition of uranium hydride UH_3 indicate that it is not a solid solution or interstitial compound, but a definite chemical compound.

5. Uranium hydride UH_3 may be thermally decomposed, yielding uranium U metal powder which is exceedingly reactive.

6. The general chemical properties of uranium hydride UH_3 are those of a strong reducing agent; it readily reacts with oxidizing agents of all types, as well as certain organic compounds. Some reactions in aqueous medium serve to prepare uranyl salts.

7. Uranium hydride UH_3 reacts with a wide variety of gases, yielding in certain cases uranium U compounds difficult to

prepare by other means. The techniques are simple, and are

recommended preparative methods.

8. Uranium metal or its hydride or certain compounds prepared

from it are conveniently employed in the purification of

several laboratory gases.

9. By mixing the finely subdivided [uranium hydride] UH_3 with other

substances also in the form of a fine powder, and heating,

the hydride is decomposed, leaving [uranium] U powder intimately

mixed with the other substance, with which it may react on

stronger heating. (For example,) when carbon black in the

proper proportion is used, uranium monocarbide is formed.

10. Employing the technique discussed above with [uranium UF_4

tetrafluoride] caused its reduction to [uranium trifluoride] UF_3,

previously unknown. The trifluoride is a black, coke-like

solid.

11. [Uranium hydride] UH_3 readily forms "amalgams"; the evidence

shows that the preparations are not true solutions in [mercury] Hg

or true amalgams, but suspensions. The amalgams vary in con-

sistency from a fluid through a semi-solid to a dark solid,

as the [uranium hydride] UH_3 concentration is raised. Air, water,

or [hydrogen sulfide] H_2S serves to cause the hydride to precipi-

tate from its amalgam.

12. Several applications of [uranium hydride] UH_3 and the hydride

reactions are: laboratory source of pure hydrogen or deuterium,

preparation of powdered [uranium] U, preparation of [uranium] U com-

pounds, isolation of intermetallic compounds of [uranium] U,

etching metallographic specimens, ████████████████████

████████, maintaining a given hydrogen or deuterium pressure,

and analysis of metallic [uranium] for the free element.

67 references/#

██

108-l-295

XI.
LITERATURE CITED

Much of this information has been collected together, forming the Manhattan Project Technical Series (MPTS), of which the Plutonium Project Record (PPR) is a division. The PPR consists of "A" volumes, which are of a text and survey nature, and "B" volumes, which contain papers written in the style of ordinary chemical journals.

1. Spedding, Wilhelm, and Keller, CT-2711 (July 13, 1945); CT-2712 (June 26, 1945).

2. Sieverts and Bergner, Ber., 45, 2583 (1912).

3. Driggs, U. S. Patent 1,816,830 (filed November 25, 1929; issued August 4, 1931).

4. Wilhelm and Gray, CC-178 (June 25, 1942).

5. Warf, Newton, Butler, Ayres, and Johns, CC-580 (April 15, 1943); CC-587 (April 19, 1943).

6. Spedding, Newton, Johns, Johnson, Daane, Nottorf, and Warf, "Preparation and Physical Properties of Uranium Hydride", Plutonium Project Record (MPTS), Volume XI B, 1946.

7. Warf, CC-803 (July 15, 1943).

8. Kirst, Nagle, and Castner, Trans. Am. Inst. Chem. Engr., 36, 371 (1940).

109-l-295

SECRET

10. Smyth, "Atomic Energy for Military Purposes", Princeton
    University Press, Princeton, N. J., 1945, pp. 116, 146.

11. Warf and Feibig, CC-1524 (March 10, 1944).

12. Plott, Hamilton, Fentress, and Inman, CT-1103 (December
    4, 1943).

13. Spedding, Warf, Newton, Johnson, Johns, Ayres, Butler,
    Fisher, and Nottorf, "The Chemical Properties of Uranium
    Hydride", Plutonium Project Record (MPTS), Volume XI B,
    1946.

14. Wheland, "The Theory of Resonance", John Wiley & Sons,
    Inc., N. Y., 1944, pp. 69, 78.

15. Warf, CC-862 (August 8, 1943); CC-1059 (October 9, 1943);
    CC-1061 (October 8, 1943).

16. Newton, Nottorf, Daane, and Johnson, CC-858 (August 7,
    1943).

17. Powell and Warf, CC-1524 (March 10, 1944).

18. Tucker and Figard, CC-1975 (September 10, 1944).

19. Burke and Smith, IA-37 (November 13, 1943).

20. Newton, CC-695 (May 26, 1943).

21. Rundle, Wilson, and McDonald, "The X-Ray Investigation
    of the Uranium-Hydrogen System; the Structure of Uranium
    Hydride", Plutonium Project Record (MPTS), Volume XI B,
    1946.

22. Schumb and Rittner, J. Am. Chem. Soc., 65, 1692 (1943).

23. Gillespie and Hall, ibid., 48, 1207 (1926).

24. Stock and Ritter, Z. physik. Chem., 119, 333 (1926).

SECRET

295

SECRET

25. Warf, "Some Reactions of Uranium Metal", Plutonium Project

    Record (MPTS), Volume XI B, 1946.

26. Warf, CC-580 (April 15, 1943).

27. Spedding, Johns, Sullivan, and Voigt, CC-765 (June 30,

    1943).

28. Ayres and Johns, "The Separation of Long-Lived Fission

    Gases", Plutonium Project Record (MPTS), Volume IX B,

    1946.

29. Warf and Feibig, CC-1504 (June 10, 1944).

30. Fisher and Warf, CC-1057 (November 6, 1943); CC-1091

    (January 7, 1944).

31. Hill and Miller, J. Am. Chem. Soc., 47, 2702 (1925).

32. Warf, CC-1194 (December 9, 1943).

33. Willems, Z. anorg. allgem. Chem., 246, 46 (1941).

34. Tevebaugh, Walsh, Iliff, and Johns, CC-1063 (November 6,

    1943); CN-1199 (December 10, 1943).

35. Warf, Raeuchle, and Ericson, CC-1504 (June 10, 1944).

36. Warf and Baenziger, "The Preparation and Properties of

    Some Mixed Uranium Halides", Plutonium Project Record

    (MPTS), Volume XI B, 1946.

37. Ayres, CN-1243 (January 8, 1944).

38. Rundle and Baenziger, CC-1524 (March 10, 1944); Newton

    and Rundle, "The Uranium-Nitrogen System", Plutonium

    Project Record (MPTS), Volume XI B, 1946.

39. Newton, CC-1524 (March 10, 1944).

SECRET
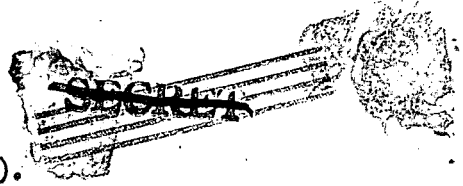
40. Warf and Nottorf, CC-803 (July 15, 1943).

41. Warf, Brown, and Wright, CC-1524 (March 10, 1944).

42. Warf, "The Preparation and Properties of Uranium Tri-
    fluoride", Plutonium Project Record (MPTS), Volume
    XI B, 1946.

43. Warf and Cline, "Pyrohydrolysis in the Analysis of
    Fluorides and Other Halides", Plutonium Project Record
    (MPTS), Volume XIII B, 1946.

44. Emeleus and Anderson, "Modern Aspects of Inorganic
    Chemistry", D. Van Nostrand Co., Inc., N. Y., 1945,
    p. 231.

45. Butler, Voigt, Wolter, and Ayres, CN-925 (September 8,
    1943).

46. Warf, CC-1059 (October 9, 1943).

47. Ahmann, Baldwin, and Wilson, CT-2960 (October 27, 1945).

48. Low, Chemist-Analyst, 29, 13 (1919).

49. Fisher and Warf, CC-1091 (January 7, 1944).

50. Warf and Ayers, CC-1524 (March 10, 1944).

51. Warf, CC-1091 (January 7, 1944).

52. Fisher and Warf, CC-1091 (January 7, 1944).

53. Goldblatt, Wright, and Warf, CC-1524 (March 10, 1944).

54. Daane, CC-1059 (October 9, 1943); Goldblatt and Warf,
    CC-1194 (December 9, 1943).

55. Johnson, CC-1059 (October 9, 1943).

56. Daane, CT-686 (May 22, 1943).

112-L-295
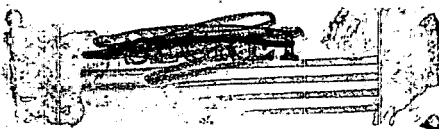
57. Johns, Butler, Tevebaugh, Wolter, and Voigt, CN-727

(June 15, 1943); Butler, CC-725 (June 15, 1943).

58. Butler and Wolter, CN-795 (July 15, 1943).

59. Butler, CC-725 (June 15, 1943).

60. Johns and Newton, CT-583 (April 5, 1943).

61. Warf, "Analysis of Metallic Uranium for the Free Ele-

ment", Plutonium Project Record (MPTS), Volume XIII B,

1946.

62. Feibig and Warf, "Determination of Water in Fluorides",

Plutonium Project Record (MPTS), Volume XIII B, 1946.

63. Rodden, CCA-1018 (November 30, 1943).

64. Ruhoff, Burnett, and Reid, "Organic Syntheses", Col-

lective Volume 2, John Wiley & Sons, Inc. N. Y.,

1943, p. 338.

65. Erdmann, Ber., 26, 1990 (1893).

66. Warf et al., Plutonium Project Record (MPTS), Volume

XIII A, Chapter 14, 1946.

67. Ayers and Warf, CC-1517 (March 14, 1944).

113-l-295

SECRET

XII. ACKNOWLEDGEMENTS

The writer wishes to express his thanks to Dr. F. H.
Spedding for his direction and supervision of the research
on uranium hydride. Acknowledgements are also due to the
following for their parts in the investigations: to Drs.
A. S. Newton, Oliver Johnson, and R. W. Nottorf for the
data on deuterium separations and the physical and thermo-
dynamic properties summarized in Part V, and for some sections
of Part VI; to Dr. R. E. Rundle for supervising the x-ray
diffraction work; to Dr. I. B. Johns and Mr. J. A. Ayres for
some of the radiochemical studies and the reactions of the
hydride with heavy metal salts; and to Mr. T. A. Butler for
portions of the early work on the hydride amalgam. Finally,
thanks are also due to Dr. J. A. Wilkinson for his assistance
in the preparation of this thesis.

Nearly all of the experimental work described was con-
ducted during the writer's employment by the Manhattan
District, Corps of Engineers of the United States Army,
contract number W-7405-eng-82.

END OF DOCUMENT

114-l-295

SECRET