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Issue Date:

June 27, 1955

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ZIRCONIUM HYDRIDE IN AIRCRAFT REACTORS

Report of a Conference at Wright Air Development Center, April 27, 1955

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by

P. T. Gilbert, Jr.

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I. PURPOSE

This meeting provided an exchange of information concerning the recent and current work on the use of hydrides of zirconium and its alloys as moderators and shields, deuterides as reflectors, and zirconium-uranium hydrides as moderator-fuel elements, in nuclear aircraft engines.

II. PERSONNEL

The following individuals attended the meeting, which was held in the Power Plant Laboratory at Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, on April 27, 1955:

From Wright Air Development Center: Capt. William McCauley, WCLPU, who acted as chairman; Lt. Victor P. Kovacik, WCLPU; Capt. Fredrick R. Westfall, WCLPU; Capt. Anthony Mione, WCRTP; Lt. Paul M. Uthe, WCRTY; Lt. T. Hikido, WCRTL-1; and the following, whom I did not meet: William C. Shiel, WCSNL; Jules I. Wittebort, WCRTY-3; William F. Studer, WCLPU; John A. Poulson, WCSN; and Jay H. Brill, WCLPU.

From Sylvania Electric Products: John L. Zambrow; Bernard Kopelman: and Harold M. McCullough.

From General Electric Co.: Garth Leeth; Earl S. Funston; and James A. McGurty.

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From Wright Aeronautical Division of Curtiss-Wright: Thomas E. Schober; Robert A. Loos; Joseph W. Sausville; and René A. Bolomey.

From North American Aviation: P. Gilbert.

III. SUMMARY OF CURRENT ACTIVITIES

A. General Electric, ANP Division, Evendale, Ohio:

Preparation of massive (100 per cent dense) hydrides of zirconium and certain other metals and alloys; preparation of massive zirconium deuteride; kinetics of hydriding. Reactor design embodying the hydrides; zirconium-uranium hydride as moderator-fuel. Density and hydrogen conten of zirconium and alloy hydrides at high temperatures; determination of hydrogen. Thermal expansion, thermal conductivity, mechanical properties of zirconium hydride, hot and cold. Fabrication; canning and cladding of zirconium hydride. Stability in air; corrosion by organic coolants.

B. Wright Air Development Center:

Reactor design and engineering embodying zirconium and alloy hydrides and liquid fuels. Calculation and measurement of dissociation pressure of zirconium hydride. Design of control rod activated by zirconium hydride.

C. Sylvania Electric Products:

Preparation of massive zirconium hydride. Hot-pressing zirconium hydride powder, and mechanical properties of compacts.

D. Battelle Memorial Institute: (for GE-ANP)

Search for alloy hydrides of high hydrogen content; thermal conductivity and physical properties of zirconium hydride.

E. Oak Ridge National Laboratory: (for GE-ANP)

Radiation stability of zirconium hydride, with respect to dissociation pressure and mechanical properties. Studies of fluoride fuel with zirconium hydride. Cross sections of pure rare earths for alloying with zirconium hydride.

F. Knolls Atomic Power Laboratory:

Extrusion canning of zirconium hydride.

G. Iowa State College, Ames Laboratory:

Production of pure rare earth metals for alloy hydrides.

IV. DISCUSSION

The following information was presented at the meeting, principally by McGurty and Leeth of General Electric, McCullough of Sylvania, and Kovacik of WADC; there were additional contributions from Bolomey of Wright Aeronautical Division, and others. The contribution from North American Aviation has been included in the General Chemistry progress reports and will not be reiterated. The material has been rearranged according to subject, for convenience in reference.

A. Preparation of Massive Hydride

1. Zirconium Hydride

a. General Electric

As an example of the GE hydriding process, a cylinder of massive zirconium hydride, 1" in diameter and 8" long, of N_H 4.2 (x 10^{22} atoms of H per cm^3), was exhibited. The larger, drilled cylinders of massive hydride, described in Memo-1360, were also shown. In the preparation of this substance, according to McGurty, machined cylinders of zirconium are brought to a temperature (2100-2200°F) above the temperature range in which hydriding will cause the zirconium to rift; the heating is done in helium or vacuum, which, after attainment of the temperature, is replaced by hydrogen (at one atmosphere). It is of particular importance to keep the metal out of contact with hydrogen during the initial heating. At the hydriding temperature, the metal and hydride are plastic, and stress-relieve themselves during the expansion that ensues on absorption of hydrogen, so that no cracks develop. An alternative procedure consists in sealing the zirconium in a capsule, heating it, and then slowly regulating access of hydrogen. After the sample has attained the composition ZrH it can be freely heated and cooled in hydrogen without danger of cracking. This hydriding technique readily yields hydrides as high as ZrH, but introduction of additional hydrogen into the massive material is very difficult, even below 1400°F, unless the pressure is increased above 1 atmosphere. The N_H of such (metastably) saturated specimens is a little over 4, but it has been pushed as high as 5.7 in a clad specimen. GE expects to employ pressures as high as 1000 psi in the effort to attain higher N_H values in the massive hydride without cracking.

b. Sylvania

The method of preparing massive zirconium hydride employed at SEP, as described by McCullough, consists in heating the zirconium in vacuum to the hydriding temperature, then admitting the hydrogen up to pressures of 2 atmospheres absolute, and cooling the sample along an isochore, i.e., reducing the pressure as the sample cools so as to maintain equilibrium with a hydride of constant composition. However, after the pressure has thus been reduced to .1 atmosphere, the hydride is cooled to room temperature without further reduction of pressure. By this method zirconium hydride has been obtained up to an N_H of 4-1/4, but no higher without cracking. Sylvania has tried very slow hydriding at 2 atmospheres up to 950-980°C followed by cooling without reduction of the hyrogen pressure, but these samples always cracked. The secret of attaining higher hydrogen content appears (in agreement with GE) to reside in the use of higher pressures rather than in manipulation of temperature.

2. Zirconium Alloy and Other Hydrides

The GE hydriding process, according to McGurty, has been employed for the preparation of massive hydrides of yttrium, cerium, titanium and uranium, alloys of zirconium with titanium, yttrium and cerium, and alloys of titanium with yttrium. Yttrium is particularly valuable in that it permits attainment of unexpectedly high hydrogen concentrations in zirconium and titanium. Whereas the limiting composition for massive zirconium hydride is slightly over ZrH, when 10 per cent yttrium is added to the zirconium a composition $(Zr,Y)H_2$ is reached without cracking.

Similarly, 10 per cent yttrium will yield (Ti,Y) $H_{1.85}$ under conditions of massive hydriding at 1 atmosphere. In the case of the titanium-zirconium alloy it had been hoped that the lowering of the transition temperature of zirconium by titanium would enhance the capacity for hydrogen; but this does not occur. Actually, seeing that hydriding takes place in the beta phase of either metal, an improved hydrogen capacity of the alloy should not have been expected on this basis.

These alloys were prepared by arc-melting. It was noted, incidently, that an oxide film does not inhibit the hydriding of the yttrium-zirconium alloy as much as it does that of pure zirconium.

3. Zirconium Deuteride

General Electric is commencing study of the preparation of massive zirconium deuteride for use as reflector in aircraft reactors.

4. Kinetics

General Electric is making preliminary studies of the kinetics of massive hydriding of zirconium, according to McGurty. Equilibration between the surface of the hydride and the ambient atmosphere (of hydrogen) seems to be very rapid. The failure of massive hydrides to reach equilibrium with hydrogen under conditions which should yield higher concentrations is ascribed to a slow reaction rate at certain stages of hydriding; but see Section B in this connection.

5. Costs

McGurty indicated the approximate costs of some of the materials required for these studies. The highly purified rare earths are obtained from Spedding of the Ames Laboratory. Yttrium oxide, purified to better than 99.99 per cent yttria (for low neutron cross section) costs $250 per pound. Yttrium metal is more costly, but its price is expected to decline to that of lanthanum, which is $200 per pound. A less pure lanthanum costs $40 per pound. Niobium, employed for cladding, costs $400 per pound.

B. Constitution of Massive Hydrides

It appears likely that the massive hydride of zirconium, apparently saturated with hydrogen under the hydriding conitions described above, is a saturated solid solution of delta hydride in beta zirconium, which has the composition ZrH or slightly above, depending on the temperature. It is not, however, saturated with respect to the gas phase: at equilibrium, compositions approaching ZrH_2 should be reached. But if hydrogen exceeding 1 mol per mol of zirconium is introduced, e.g., by increasing the pressure over the massive hydride, a second phase (delta zirconium hydride) begins to form and the material is no longer homogeneous at the hydriding temperature. Generally, this two-phase mixture tends to crack as it absorbs hydrogen. Samples of massive hydride which have been obtained exceeding ZrH in hydrogen content are hard and brittle, resembling cast iron. This difference between ZrH and higher massive hydrides may be understood in view of the fact that although at room temperature both materials are a mixture of alpha zirconium and delta hydride, presumably containing some of the little-known gamma phase (possible Zr_2H), ZrH at room temperature should be a somewhat hypereutectic mixture of alpha and delta whereas at N_H 5.7 the material is almost entirely delta, probably a somewhat substoichiometric Zr_2H_3. The matrix of eutectoid alpha-delta mixture evidently allows retention of the metallic properties of alpha zirconium.

By contrast with zirconium, cerium exhibits no corresponding high solubility of the hydride phase in the hot metal, and the massive hydride, which is readily carried to N_H 5.6 at 1500°F, is a two-phase mixture at all temperatures. Massive cerium hydride is very different from ZrH, resembling lead in appearance. Further, it is pyrophoric in air at room temperature, a block of the material growing steadily warmer until it catches fire. Massive zirconium hydride, on the other hand, is remarkably inert (See Section F-1).

G. Hydrogen Content.

1. Zirconium Hydride: As mentioned, the highest massive zirconium hydride thus far obtained has N_H 5.7. The N_H values are calculated from the weight percent of hydrogen and the density. Complete information on the interconversion of per cent hydrogen, atomic ratio,

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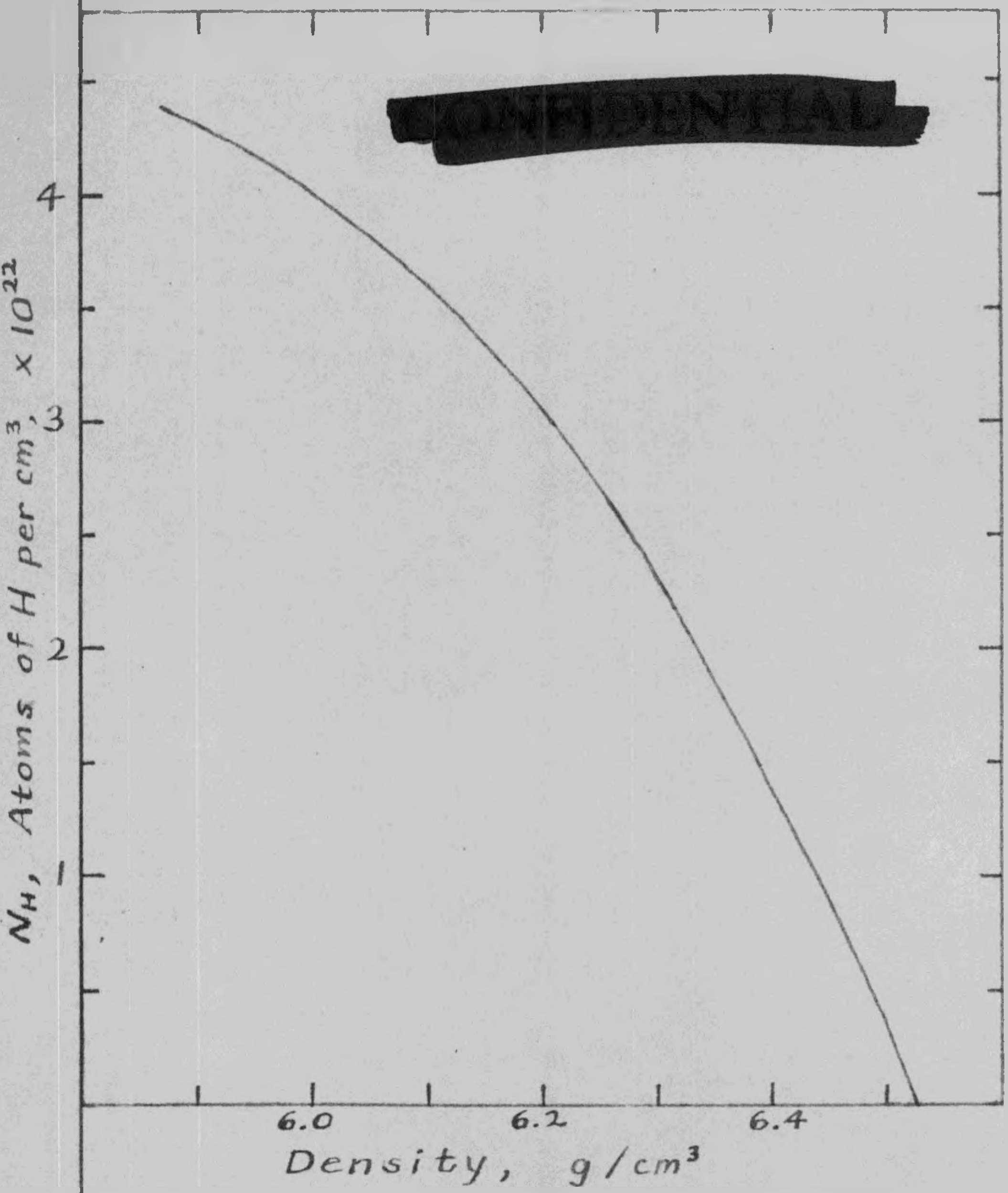
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Fig. 1. Hydrogen Content and Density of Zirconium Hydride.

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N_H, and density was not presented at the meeting, but can be calculated on the basis of density data available from General Electric on request. McGurty did, however, show a graph of N_H vs. density for zirconium hydride, up to N_H 4.3. The data were copied and have been carefully reproduced in Fig. 1. Estimation of N_H at elevated temperatures is done by means of densities corrected for expansivity (See Section E-1).

A function of considerable importance in aircraft reactor design is the maximal practical hydrogen content of massive hydride as determined by hydriding temperautre. The data are quoted as N_H versus temperature at 1 atmosphere (or 15 psia) and thus represent a sort of isobar. It is not, however, in general an equilibrium isobar; at the higher temperatures it may conicide with the equilibrium 1-atmosphere isobar, but at the lower temperatures the hydrogen solubility is limited by considerations discussed in Section B. Whereas this isobar is of value in predicting the N_H to be expected under operating conditions in a reactor, the possiblity that the indicated N_H may be exceeded by closer approach to thermodynamic equilibrium must not be forgotten. It will be a matter of interest to correlate the practical N_H data being gathered by GE with the true thermodynamic isobars insofar as these are known; this has not yet been carefully done. Graphs showing the practical N_H as function of hydriding temperature for zirconium hydride were presented by McGurty, and the data have been consolidated and reproduced in Fig. 2.

2. Hydrides of Yttrium, Titanium and Alloys: No density data were presented, but, as mentioned, they can be obtained (as a function of temperature) for the materials in question from General Electric. The graphs of practical N_H of massive hydrides vs. hydriding temperature reveal the superiority of the yttrium-containing alloys. Ten per cent yttrium will yield massive hydrides of the composition $(Zr,Y)H_2$ and $(Ti,Y)H_{1.85}$. This yttrium content is more favorable than 25% yttrium with respect to retention of hydrogen at intermediate temperatures; pure yttrium can be massively hydrided as far as $YH_{1.5}$. The highest N_H value yet recorded for a massive metallic hydride is that for the 10% yttrium-

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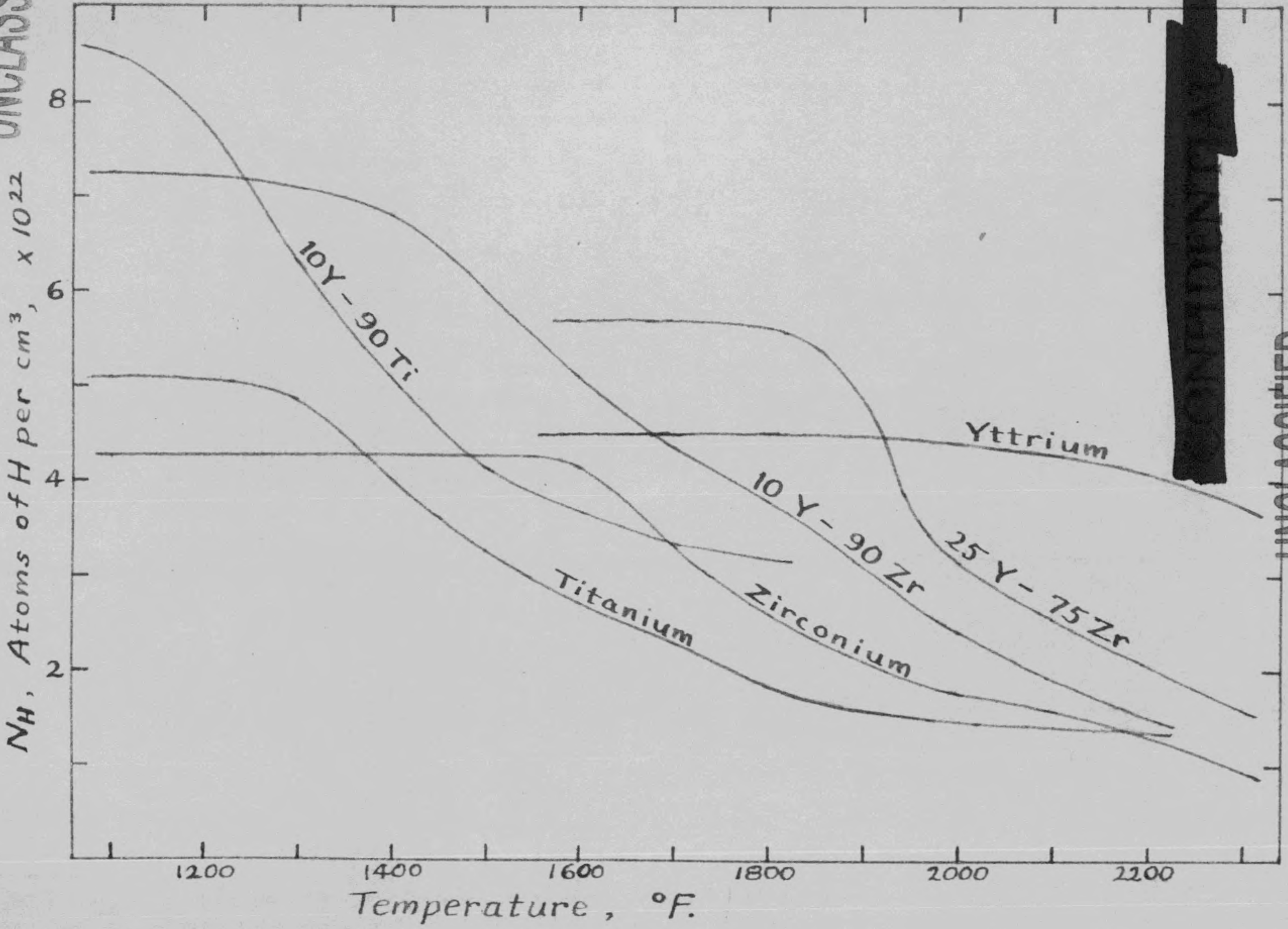

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Fig. 2. Hydrogen Content as Function of Hydriding Temperature for Various Massive Hydrides.

titanium alloy, viz., 8.7. The 10% yttrium-zirconium alloy goes to an N_H of 7 to 8. McGurty's charts showed maximal massive N_H data for yttrium, titanium, 10% yttrium-zirconium, 10% yttrium-titanium, and 25% yttrium-zirconium; these data are shown in Fig. 2 along with those for zirconium. It will be seen that at the highest temperature, beyond the inflections (for the other metals) which, on a thermodynamic isobar, should be vertical and correspond to a two-phase mixture in a two-component system, yttrium contains the most hydrogen, about three times as much as titanium or zirconium, the yttrium alloys lying between. The temperatures at which N_H begins to drop markedly vary widely, and cannot be obtained for the alloys by interpolation between the pure metals. The 10% yttrium-titanium, 10% yttrium-zirconium, 25% yttrium-zirconium, and yttrium hydrides enjoy each a certain temperature range of superiority over the rest; the pure hydrides of titanium and zirconium are no where superior to all of the alloys.

3. Determination of Hydrogen: The following method, described by McGurty, has been in use at GE for measuring the hydrogen content not only of the massive hydrides, but also of such materials as lithium hydride, borohydrides, and titanium metal of low hydrogen content (in the ppm range). A sample weighing .2 to .4 gram is mixed with 4 to 5 times its weight of granular tungsten and heated by induction in a magnesia boat in a Lindberg furnace of the type used for carbon determination. A temperature of 1700 to 1800°C is employed, and the expelled hydrogen is carried off in a current of helium, passed over a desiccant to catch any water evolved as such, then over hot copper oxide to oxidize the hydrogen to water, and finally over a second desiccant; the water is determined by weighing. The method takes 15 minutes.

The hydrogen content of massive hydrides is sometimes determined, depending on feasibility, by weight increase, by measurement of density, or by combustion to oxide. Vacuum fusion is also employed for the determination of hydrogen.

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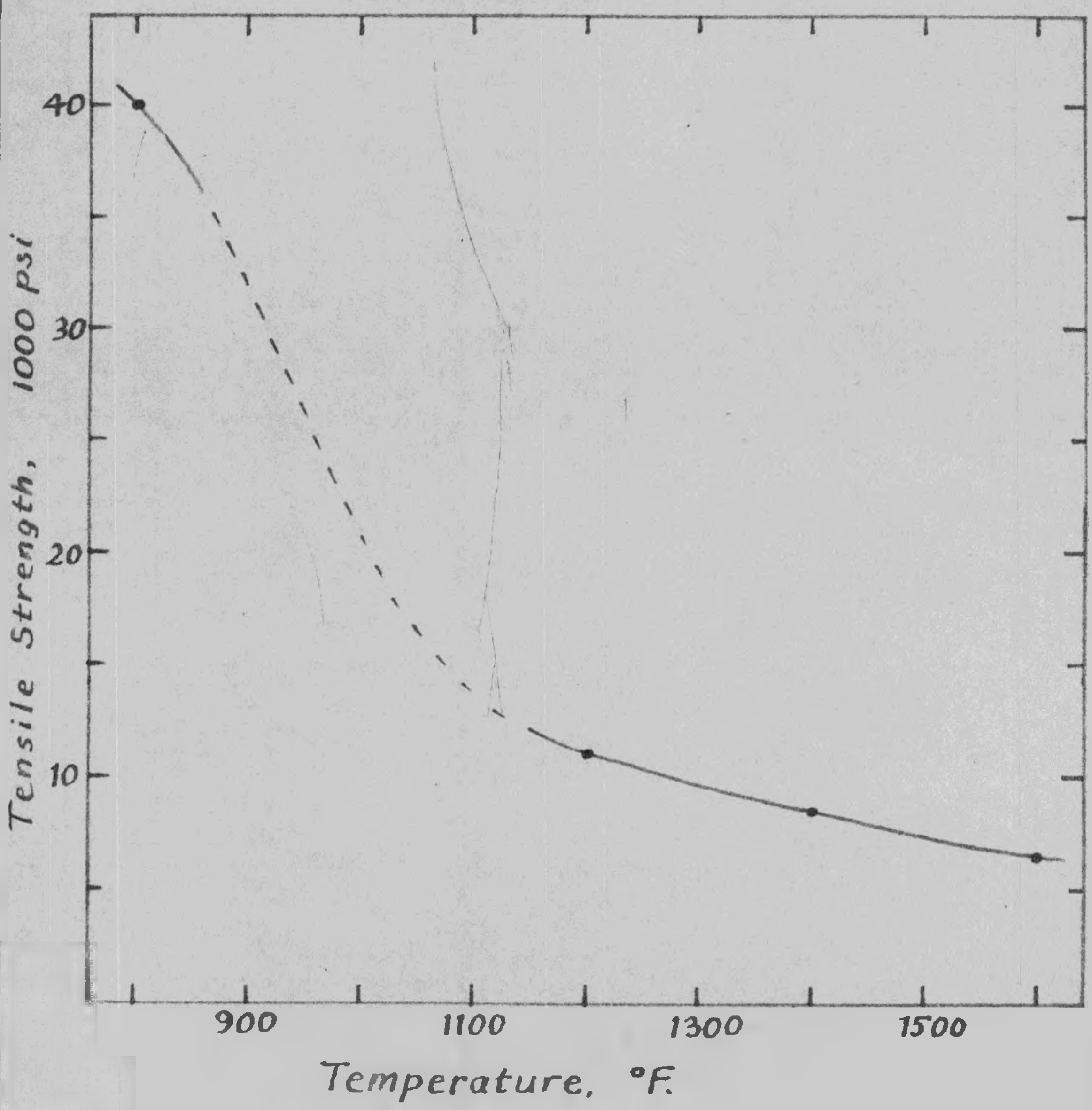

Fig. 3. Tensile Strength of $ZrH_{1.1}$

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D. Mechanical Properties:

1. Hardness: According to McGurty, massive zirconium hydride has a hardness at room temperature of 35 to 39 Rockwell C, depending on the rate of cooling.

2. Elasticity: The elastic modulus of massive zirconium hydride is said to have been measured at GE.

3. Compressive Strength: As reported by McCullough, massive zirconium hydride of N_H 4 exhibited a compressive strength of 198,000 psi. The compressive strength of hot-pressed zirconium hydride of N_H 5.65, density 4.92 (20% void), pressed at 560°C under 25 tsi, was 41,000 psi. Cold-pressed and sintered zirconium hydride was too weak to be of interest.

4. Ductility: Hot-pressed zirconium hydride of the above description has almost no cold ductility. Massive ZrH, in the form of tensile specimens, according to McGurty, shows 5% deformation followed by brittle fracture, at 800°F; above 1200°F the hydride (now in the beta phase) is plastic. Photographs were shown of the broken specimens; at 1400° they necked down and exhibited ductile fracture.

5. Tensile Strength: The tensile specimens are prepared by machining the zirconium and hydriding it massively by the GE process. Above 800°F the hydride is somewhat stronger than zirconium, but this strength at best is not high. Fig. 3 shows the tensile strength of $ZrH_{1.1}$ (N_H4.2) as a function of temperature. By way of comparison, the strength of zirconium at 1500°F is 3200 psi, less than half that of the hydride.

E. Thermal Properties:

1. Expansivity: General Electric has measured the expansivity of massive ZrH from room temperature up past the transition temperture; these results are adequately reported in APEX-14. Below the transition temperature it matches the expansivity of type 446 stainless steel fairly closely, being nearly twice that of zirconium. At the transition, there is a marked shrinkage of volume.

2. Thermal Conductivity: This property is being measured at Battelle for GE. According to McGurty (see also APEX-14), the conductivity of massive ZrH is close to that of zirconium; it should be noted, however, that zirconium is not a particularly good conductor. The conductivity of ZrH is observed to decrease from room temperature up to the alpha-beta transition, whereupon it increases. The Battelle tests showed that at 1800°F the hydride had twice the room-temperature conductivity, but the sample in question, which was in an atmosphere of helium, may have lost hydrogen; confirmation is not yet available. Measurements at GE showed the conductivity of the hydride to be just above that of zirconium, and to drop 20% in going from room temperature to 1400°F.

3. Dissociation Pressure:

a. General Electric: Data reported by McGurty for massive hydride of N_H 4.2 are given in Table I. According to Fig. 1, this hydrogen content is equivalent to 1.18% and a formula of $ZrH_{1.08}$. Applying these dissociation pressures to the isochore chart given in NAA-SR-1205, one finds that they correspond to X = .99 to 1.00 ($ZrH_{.99}$ to $ZrH_{1.00}$), and that whereas the last three data are for the beta phase, at 1400°F some delta phase should appear and the isochore lies in the two-phase discontinuity. This is accurately borne out by the dissociation pressure of 1.0 psia. Thus, aside from discrepancy of .08 in X (the H/Zr ratio) these results agree with earlier work.

Table I.

Dissociation Pressure of $ZrH_{1.08}$

Temperature	Pressure
1400°F	1.0 psia
1500	2.9
1600	7.
1700	14.

b. Wright Air Development Center:

Dissociation pressure of massive zirconium hydride is being measured also at WADC. Data presented in graphical form by Kovacik are reproduced in Table. II. These are for

Table II

Dissociation Pressure of $ZrH_{.49}$

Temperature	Pressure
1500°F	0.42 psia
1600	0.87
1700	1.75
1800	3.41

(continued next page)

1900°F	6.28 psia
2000	10.9
2100	18.0
2200	27.2

a hydride of N_H content reported as 2.18 and X = .490. However, there appears to be a discrepancy here, inasmuch as the density chart (Fig. 1) implies that N_H = 2.18 is equivalent to X = .526, while X = .490 is equivalent to N_H = 2.03; this discrepancy cannot be resolved without further inquiry. If the pertinent equation for the dissociation pressure of beta-phase zirconium hydride, given in NAA-SR-1205, is applied to these data, the calculated values of X decline from .51 at 1500°F to .40 at 2200°F. The implication is that the partial molal heat of solution of hydrogen in beta zirconium, as found at WADC, is less than the best average value deduced from earlier work. On the whole, however, agreement is good, and these measurements are carried to higher temperature (1200°C) than any others heretofore reported except by Sieverts, who worked with impure material.

Kovacik has employed the data of Hall, Martin and Rees together with ours (NAA-SR-1205) in constructing extensive isochore and isotherm charts for the zirconium-hydrogen system, which he has used in evaluating and comparing their measurements and those of GE and calculating the behavior of the hydride under reactor conditions. In the apparatus employed at WADC for the dissociation pressure measurements, the samples were contained in a capsule which they filled nearly completely, in order to minimize the correction for the hydrogen present in the gas phase. The capsule was further surrounded by hydrogen at the same pressure as that which prevailed within, in order to obviate diffusion. Measurements were carried as high as 30 psia, these being the first for zirconium hydride above 1 atmosphere thus far reported, except for ours. Kovacik reported results obtained with a sample of N_H 4 at temperatures up to 1950°F, but he indicated that experimental difficulties were encountered; the data as plotted show what looks like a large gas space correction, the slope of the isochore being too small. Work is in progress and further measurements of dissociation pressure are expected.

4. Critical Temperature: An interesting point, discussed by several members of the meeting, concerns the possibility that a critical solubility temperature (consolute temperature or temperature of complete miscibility) exists in the zirconium-hydrogen system for the beta and delta phases. Kovacik, who has studied the statistical-mechanical evaluation of Martin and Rees (Trans. Faraday Soc., 50, 343 (1954)) and has carried out machine calculations and extrapolations based on the data of Hall, Martin and Rees, believes that the beta and delta phases should become miscible at about 1640°F or 1150°K. Bolomey of Wright Aeronautical Division was inclined to agree. The fact that these phases are respectively cubic body-centered and cubic face-centered was considered to offer no serious obstacle. However, I challenged these conclusions, because the data of Hall et al are not very good for the purpose of defining the phase boundaries at higher temperatures, and because the more accurate data of Edwards, Levesque and Cubicciotti (J. Am. Chem. Soc. 77, 1307 (1955)) show very clearly that the boundaries of the two-phase region are converging only slowly and are still widely separated at 1150°K. It seems more likely that if a consolute temperature exists below the melting points, it occurs at unattainably high hydrogen pressures.

F. Chemical Properties:

1. Reaction with Air: Massive zirconium hydride is surprisingly stable in air at elevated temperatures. According to McGurty, unclad massive ZrH shows no appreciable loss of hydrogen in air below 1500°F. If the hydride has been prepared by hydriding at 1650°F (N_H 4; see Fig. 2), its dissociation pressure at 1500°F (Table I) is not sufficient for the hydrogen to penetrate the thin oxide film which forms. It is to be noted that the oxide film presents an excellent barrier to both ingress and egress of hydrogen; after 100 hours in air at 1500°F, massive ZrH is oxidized to a depth of only .02 inch. Below 1100°F the hydride is stable in air indefinitely.

2. Reaction with Metals: As will be noted in Section I-1, no oxidation-resistant metal suitable for canning has been found which does not react with massive zirconium hydride at temperature above those at which the hydride is sufficiently stable in air. It alloys with stainless steels and with Inconel; at 2000°F Inconel forms an alloy which is too hard to be cut with a hacksaw. On the other hand, the hydride is inert to molybdenum and niobium at these temperatures.

3. Corrosion by Liquids: McGurty reported that GE is testing the corrosion of massive ZrH by organic coolants as 600-700°F in connection with its use in aircraft reactor shields. It appears that the hydride can probably run for thousands of hours in these liquids without detriment.

GE is also interested in the corrosion of aircraft reactor shield hydrides by liquid salt coolants. No data have been reported yet. In answer to a question, it was stated that corrosion of zirconium hydride by liquid sodium has not been studied.

According to McCauley, ORNL is testing zirconium hydride moderator slugs, canned and uncanned, in contact with UF_3-containing fluoride fuel (Funazr). Optimism concerning this system was expressed. Bolomey pointed out that if the UF_3 disproportionated, yielding metallic uranium, this could adversely affect the zirconium hydride; but McCauley replied that UF_3 does not disproportionate much below 1250°C and the hydride should be safe from this effect.

G. Nuclear Properties:

1. Cross Sections: With respect to neutron absorption, the macroscopic cross section for zirconium is generally given as $.008\ cm^{-1}$. Additions of yttrium and cerium will affect this property adversely, but not severely. Yttria of better than 99.99% purity, having a cross section (for yttrium) a little below the $.036\ cm^{-1}$ reported previously, on exposure to pile radiation to burn up impurities, showed hardly any decrease in the cross section. Ames is preparing some yttrium metal for these studies, having a purity in excess of 99.999%. The cross section of cerium ($.021\ cm^{-1}$) is close to that of niobium, whereas praseodymium,

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which is more detrimental, resembles stainless steel or titanium in this respect. The use of praseodymium in the moderator bodies is discouraged for this reason.

2. Radiation Stability: McGurty reported that massive zirconium hydride had been tested in the HB -2 hole of the LITR at ORNL, a temperature of 1500°F being produced by the gamma and neutron heating. The dissociation pressure was measured (up to 1 atmosphere) as a function of temperature during thermal cycling in which the temperature was controlled by air cooling. In order to study the effects of irradiation, the 1-1/2" cylindrical specimen of ZrH, with a thermocouple at the center, was subjected to heating and cooling with and without irradiation. The cooling characteristics of the specimen were found to remain unchanged under irradiation during three weeks, implying that the thermal conductivity, at least, was unaffected, and that probably no cracks developed. To date, however, the specimen has been too radioactive for further examination.

H. Fabrication:

1. Cold Compacting: McCullough said that zirconium hydride cold-pressed and sintered (without loss of hydrogen) was worthless as compared with hot-pressed or massive hydride, with respect to mechanical properties. It must be admitted, however, that cold-pressed compacts can be prepared with a higher hydrogen content than the best massive zirconium hydride having no alloying additions.

2. Hot Pressing: In September 1954, Hausner of Sylvania showed us some hot-pressed, machined compacts of zirconium hydride which represented the first samples successfully prepared by this technique. Since that time, according to McCullough, hydride compacts with an N_H up to 5.65 have been prepared by pressing in an Inconel-X die at 560°C under 25 tsi in one atmosphere of hydrogen. McCullough stated that these compacts had a density of 4.92, which is 80% of theoretical. However, these figures are contradictory, as they imply a density of 6.15 for the equivalent massive material, which is too high. If the

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density is really 4.92, the porosity should be nearer 15% than 20%. In any event, the compacts are much weaker than equivalent massive hydride, and no further attention is being given to hot pressing. Properties of these compacts at elevated temperatures have not been measured.

3. Machining: Hot-pressed hydride machines like graphite, having almost no cold ductility. Massive zirconium hydride can be machined satisfactorily with a carbide tool, but it is more easily formed by grinding, to which it is highly amenable.

I. Cladding:

1. Materials: Whereas massive zirconium hydride can operate in air up to 1500°F (Section D-1), intended use at higher temperatures imposes the necessity of cladding or canning. Since no suitable oxidation-resistant alloys are known which are compatible with zirconium hydride at these temperatures, a double sheath is necessary, the inner one, composed of molybdenum or niobium or an alloy of these, providing protection from the outer sheath, which is made of type 446 stainless steel or an iron-chromium-aluminum alloy. The latter seems preferable to stainless steel both chemically and with respect to neutron absorption, and its thermal expansivity is of a satisfactory magnitude. The molybdenum or niobium provides, in addition, a barrier to the passage of hydrogen; molybdenum is particularly impermeable, and effectively contains hydrogen at 2100-2200°F.

2. Hydriding in Sweater: Two techniques for cladding hydrides have been developed at GE, and were described by McGurty. In the first, the cylinder of zirconium to be hydrided is slipped into a molybdenum or niobium tube, which in turn is inserted into a tube of the oxidation-resistant alloy, and the assembly is then hydrided massively according to the GE process. The zirconium expands about 10% by volume during this process, stretching the two tubes which surround it and thereby creating an excellent bond. Clad hydrides with N_H as high as 5.5 to 5.7 have been prepared in this way. They exhibit no hydrogen loss after 100 hours at 1650°F, and no visible change. Of four samples

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(having an N_H probably below 5.5), canned by this method and heated at 1800°F for 100 hours, two remained apparently unchanged while two had shrunk away from their sheaths, evidently having lost hydrogen. The actual hydrogen content of these specimens has not yet been measured.

3. Cladding by Extrusion: In the second method, an assembly is prepared comprising a cylindrical billet of zirconium 3-1/2" in diameter and 6" long, having a 1/4" axial hole filled with copper, and surrounded by sheaths of niobium and type 446 stainless steel, the latter being coated by a sheath of copper. The assembly is then extruded at 750 - 800°C into a 3/4 inch die, providing a 20-to-1 reduction of cross section. A force of 500 tons is required; extrusion occurs very abruptly. After extrusion the copper sheath is removed with nitric acid, and the soft-center pilot of copper is removed to provide an axial hole for the introduction of hydrogen in the subsequent hydriding process. The sheaths of niobium and stainless steel are respectively .010 and .015" thick. Molybdenum would be preferred to niobium, but tubing of the requisite size is not easily available; it has been prepared by hogging out solid molybdenum rod. It is hoped that welded molybdenum-titanium alloy tubing will become available. It will be seen that the bonds in the clad assembly are wrought, but the outer surface of the stainless steel is severely fluted or scored, because the copper is too soft to pilot it smoothly. No high-temperature tests of these clad compacts were reported.

J. Alloy Hydrides: Information presented at the meeting concerning the various alloys which have been massively hydrided at General Electric is summarized here; further details are reported in the pertinent sections.

1. Yttrium: Data on hydrides of alloys of yttrium and zirconium have appeared in APEX-13 and APEX-14. McGurty reported that 5 to 10% of yttrium in zirconium provides the most favorable properties. (See Sections A-2, C-2.) Pure yttrium can be massively hydrided to $YH_{1.5}$. Ten percent yttrium in titanium will yield on N_H of 8.7, the highest known for a massive hydride. For data, see Fig. 2.

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2. Lanthanum: General Electric is trying lanthanum as an alloying constituent of zirconium in its massive hydride program.

3. Cerium: Data on hydrides of cerium-zirconium alloys are reported in APEX-13. McGurty stated that massive cerium hydride melts at about 1100°C. With respect to hydrogen content, cerium appears to be a less favorable alloying constituent for zirconium than yttrium is.

4. Titanium: McGurty reported that alloys of titanium and zirconium had been massively hydrided, but that the hydrogen content of the alloys showed no particular advantage over that of the hydrides of the pure metals. No information was available on the physical properties of the titanium-zirconium hydrides. Titanium-yttrium alloys have also been hydrided (Section J-1).

5. Uranium: An alloy of zirconium containing 4% uranium has been massively hydrided by the GE process at 1600°F to an N_H of 3.7, which is lower than the hydrogen content that can be attained in the absence of uranium. The uranium is desired for purposes of gamma shielding. It was further stated by McGurty that zirconium-uranium alloys containing as much as 60% of uranium could be hydrided without powdering. Leeth indicated that zirconium-uranium hydrides were being used in shaped wire fuel-moderator elements for intermediate aircraft reactors.

K. Application:

1. Inhibition of Corrosion: McGurty alluded to work carried out at Oak Ridge, regarding the use of zirconium and zirconium hydride for precipitating nickel and chromium impurities from the ANP liquid fluoride fuel Funazr, and for reducing uranium tetrafluoride in the fuel to the trifluoride. In this way, corrosion of the Inconel container can be considerably reduced. However, attempts to measure the solubility of zirconium hydride in the liquid have shown the hydride to be essentially insoluble.

2. Moderator in Aircraft Reactors: The design of aircraft reactors employing zirconium hydride as moderator is discussed in APEX-14. The material under immediate consideration is massive zirconium hydride of composition approximately ZrH, and the principal effort is being concentrated

upon it. McGurty believes that it is certain that either zirconium hydride or a low yttrium-zirconium hydride will be employed. He expressed the unofficial opinion that a reactor powered by uranium oxide fuel with ZrH moderator slugs would be ready to fly within two years. In these advanced designs operating temperatures of 1100°C are proposed. In order to attain stability together with high hydrogen content at these temperatures, the yttrium alloys will probably be favored. Cerium hydride melts at too low a temperature, although, as an alloying constituent, cerium increases the neutron cross section less than does yttrium.

3. Moderator-Fuel Combination: McGurty also mentioned the use of a low uranium-zirconium alloy or uranium-yttrium alloy, hydrided, for use as a moderator-fuel combination. Leeth discussed briefly the shaped wire fuel moderator elements being developed at GE-ANP. These consist of a hydrided uranium-zirconium alloy, arranged to provide a high surface-to-volume ratio, with at most 60 to 70% void in the core. The reactor is intermediate, and temperatures exceed 2000°F. An N_H above 4 is desired in the moderator, to minimize the critical mass, but a hydrogen content of this magnitude may be difficult to attain under these conditions in the uranium alloy.

McCauley stated that work at WADC indicated that a uranium-zirconium hydride fuel-moderator with circulating coolant for use in aircraft engines would entail too steep a thermal gradient at operating powers. For the power density desired, he said, a liquid fuel is required.

4. Shielding in Aircraft Reactors: McGurty outlined the subject of aircraft reactor shielding by metallic hydrides cooled by organic liquids. Various neutron absorbers (such as gadolinium and samarium) and heavy metals for gamma absorption have been incorporated. Lanthanum will also be tried for shielding. A massive 4% uranium-zirconium hydride is promising, but its hydrogen content is lower than that of pure zirconium hydride. A high uranium content is desirable for gamma shielding. If zirconium deuteride is used as reflector, it will provide gamma shielding close to the core and thus enhance the ground-safety of the shield. In a further discussion by Leeth, it was indicated that titanium hydride in the shield will scarcely provide ground-safety after shutdown. He suggested that a heavy metal hydride, perhaps

massive titanium-uranium hydride, close to the core, would be useful for this purpose. The shield will operate below 1000°F if a zirconium deuteride reflector is interposed between it and the core; several inches of zirconium will remove most of the gamma heating that would otherwise raise the shield to a higher temperature. The organic coolants, probably alkylbenzenes, will operate at 800°F; terphenyls do not have a sufficiently high N_H for this application, in which the coolant acts also as a moderator. A further possibility in which GE is interested is the use of liquid salts as coolants for hydride shields.

5. <u>Reflector in Aircraft Reactors:</u> As mentioned above, zirconium deuteride is proposed as a neutron reflector surrounding the core. General Electric is starting a study of the preparation of massive deuteride approximating ZrD in composition.

6. <u>Control Rod:</u> Kovacik described a device being built at WADC, which consists of a hydride-activated control-rod mechanism with a negative temperature coefficient. A piston attached to the control rod moves in a vertical cylinder containing an atmosphere of hydrogen; the lower face of the piston consists of massive zirconium hydride. A throttled by-pass valve connects the spaces of the cylinder above and below the piston. If, as the temperature changes, hydrogen is liberated or absorbed slowly, the pressures on the two sides of the piston remain nearly equal, as the hydrogen flows through the by-pass; and the piston will not rise from its lower position. But if, in consequence of a burst of radiation, the hydride heats too suddenly, the liberated hydrogen cannot flow through the throttle rapidly enough, and the piston will rise. If the radiation level is there-by reduced, evolution of hydrogen will cease or be reversed, and the piston will fall as hydrogen equilibrates through the throttle. A gradual increase of radiation, however great, will not move the piston, which responds only to surges of radiation. The kinetics of the device have not been worked out.

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