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Progress Report

Studies of The Rare Earth Hydrides

Technical Report 2

Physical Sciences Division

Project No. NR 336-299

Contract No. Nonr 223 (93)

Period Covered

1 October 1952—15 November 1953

by

James C. Ward, Project Supervisor

and

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at

The Department of Chemistry
University of Southern California
Los Angeles 7, California

November 15, 1953

Progress Report

STUDIES OF THE RARE EARTH HYDRIDES

Technical Report II

Physical Sciences Division: Project No. NR 356-290
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by

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in

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ABSTRACT

The chemical literature indicates that the solid hydrides of metals behave differently toward mercury, this behavior depending to some extent on the bonding type. The ionic hydrides are not affected by mercury at room temperature. Of the two metallic hydrides which have been investigated, one, uranium hydride, is wetted by mercury without a change in temperature, forming a stable dispersion, while the other, palladium hydride, is wetted exothermically.

In the present study, the surface of coarse cerium hydride was found to be wetted by mercury, forming a heterogeneous mass. The pulverized hydride was "amalgamated" to form a uniform dispersion, with a strong tendency to adhere to glass. Lanthanum hydride behaved similarly. Cerium hydride dispersions decomposed into hydrogen and cerium amalgams above approximately 115°, and reacted vigorously with water at room temperature. On exposure to air, dilute dispersions oxidized to cerium(IV) oxide, while the more concentrated preparations oxidized in part, and precipitated the unchanged hydride in part. Freezing and cooling curves of uranium hydride and cerium hydride dispersions showed no depression of the freezing point of the mercury. Filtration of cerium hydride dispersions through sintered glass removed nearly all of the dispersed phase, and gave a filtrate 0.008 per cent in cerium hydride. An indication of the maximum particle size of the cerium hydride in the filtrate is obtained from the 5/4 maximum pore size of the sintered glass filter.

A brief status report on the dissociation pressure studies is presented. A high-temperature furnace thermostatted at 750-1000° for use in this work is described. A silica torsion balance to be used in measuring compositions of solid phases in these investigations is reported. Finally, the status of X-ray diffraction work with the rare earth hydrides is given.

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I. DISPERSIONS OF RARE-EARTH HYDRIDES IN MERCURY

Introduction and Literature Survey

The behavior of hydrides of metals toward mercury is quite varied, and the evidence to date indicates that such behavior may afford a probe into the constitution of hydrides. Following are a literature survey of this topic and a phenomenological account of rare earth hydride "amalgam" studies.

The Action of Mercury on Metal Hydrides.

Lithium hydride was treated with mercury by Moers (1), who observed

(1) K. Moers, *Z. anorg. allgem. Chem.*, **113**, 191 (1920).

the evolution of hydrogen and the formation of lithium amalgam. The reaction was slow at the boiling point of mercury, and there was no particular interaction at room temperature. Lithium hydride is considered essentially ionic on the basis of structural and density considerations, liberation of hydrogen at the anode on electrolysis of the melt, optical properties, neutron diffraction studies, and especially enthalpy and Born-Haber cycle calculations. The decomposition of lithium hydride, and also of calcium hydride, by mercury, has been confirmed by Gibb (2), but no other alkali

(2) Private communication from T. R. P. Gibb, Jr. (1950)

metal or alkaline earth metal hydride seems to have been investigated in this regard. Gibb further noted that lithium aluminum hydride and its ethereal solutions are stable toward mercury up to 52°.

Mention should be made of ammonium amalgams (3), as these represent

(3) General references are available in J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IV, Longmans, Green and Co., London, 1923, p. 1005ff.

hydride amalgams, at least from one viewpoint. The constitution of

ammonium amalgams is not well understood, but it may be that N-H-Hg bonding plays a role in their stabilization (vide infra). This hypothesis is weakened, however, in that tetramethylammonium amalgams (4) are even more

(4) H. N. McCoy and W. C. Moore, *J. Am. Chem. Soc.*, 33, 273 (1911).

stable, and exhibit pronounced metallic properties. The freezing point of mercury is depressed in ammonium amalgams (5), as in the case of alkali

(5) E. M. Rich and M. W. Travers, *J. Chem. Soc.*, 1906, 872.

metal amalgams; the ammonium radical seems to form a true solution. There is also a large decrease in the surface tension of mercury upon incorporation of ammonium radicals (6).

(6) R. J. Johnston and A. R. Ubbelohde, *J. Chem. Soc.*, 1951, 1731; R. J. Johnston and A. R. Ubbelohde, *Proc. Roy. Soc. (London)*, A206, 275 (1951).

Oxley (7), on the basis of investigations of the magnetic suscepti-

(7) A. E. Oxley, *Proc. Roy. Soc. (London)*, A101, A, 277 (1922).

bility of the palladium-hydrogen system, recognized a similarity in electron structure between a metal containing hydrogen in a 1:1 atomic ratio and the metal of one higher atomic number. This hypothesis was extended by Ubbelohde (8,9), who considers that the bonding in a metal hydride MH_n

(8) A. R. Ubbelohde, *Proc. Roy. Soc. (London)*, A159, A, 304 (1937).

(9) A. R. Ubbelohde, *J. Chem. Soc.*, 1950, 1143.

behaves, with regard to further metallic bonding, approximately like the atom whose atomic number is n higher than that of M . Thus NH_4 and OH_3 amalgams are expected to resemble Na amalgams, and PdH is expected to resemble Ag.

There is general agreement in modern theories of the metallic state that the metal-metal bonding is electron-deficient and covalent in character, and that free lattice electrons, responsible for luster and conductivity, are quantized into energy bands and Brillouin zones; there is some controversy on the application of resonating-valence-bond theory to metals (10).

-
- (10) For example, see R. Kronig, "International Conference on the Physics of Metals", Martinus Nijhoff, The Hague, 1949, p. 1; L. Pauling, *ibid.*, p. 23. Also L. Pauling and F. J. Lwing, *Rev. Mod. Phys.*, 20, 112 (1948); L. Pauling, *Proc. Roy. Soc., (London)*, A196, 343 (1949).
-

Similar ideas can be extended to metal-hydrogen systems and to metal hydrides which retain metallic characteristics, e.g., luster and conductivity.

Uranium hydride is a compound manifesting metallic character, although metal-metal bonding is unimportant in its structure (11). Warf et al. (12)

-
- (11) R. E. Rundle, *J. Am. Chem. Soc.*, 73, 4172 (1951).
 (12) J. C. Warf, A. S. Newton, T. A. Butler, and F. H. Spedding, *Nucleonics*, 4, No. 3, 43 (1949)
-

found that it formed pseudo-amalgams, i.e., the hydride surface was tenaciously wet by mercury, apparently through "metallic" bonding. The amalgams were evidently not true solutions, but dispersions ranging from solids through gels to liquids, depending on concentration. The amalgamation process evidently depressed the mercury-glass interfacial tension, as strong adherence to the glass was noted, forming mirrors. There was no heat effect on amalgamation, in contrast to treatment of finely-divided uranium with mercury, which reacted to form intermetallic compounds. Other metals also were observed to wet uranium hydride.

Paal and Steyer (13) showed that mercury extracted aqueous colloidal

-
- (13) C. Paal and H. Steyer, *Ber.*, 51, 1743 (1918).
-

palladium hydride. Ubbelohde (8) found that palladium hydride ($\text{PdH}_{0.6}$) was wetted rapidly by mercury, evolving considerable heat and some hydrogen. Both palladium amalgam ($\text{PdHg}_{5.2}$) and the hydride amalgam ($\text{PdH}_{0.15}\text{Hg}_4$) were diamagnetic, suggesting that the d orbitals of palladium were saturated. Mercury was found to wet palladium, iron, and platinum after these metals, immersed in aqueous solutions, were connected to a cathode; this was ascribed to the formation of metallic bonds between the mercury atoms and the surface hydride groups, produced by electrolysis.

There is no mention of the interaction of the hydrides of the rare earth metals with mercury in the chemical literature. The metallic character of these hydrides would lead one to anticipate a behavior toward mercury resembling that of uranium hydride or palladium hydride.

Experimental

The Behavior of Cerium Hydride Toward Mercury

Preliminary tests showed that a small specimen of cerium hydride, approximating $\text{CeH}_{2.7}$ in composition, and resembling coarsely-powdered graphite in appearance, was slowly wet in vacuum by mercury without evolution of heat. The wetting of cerium hydride by mercury at room temperature affords verification of some degree of metallic character in the rare earth hydrides, and in this respect they resemble uranium and palladium hydrides rather than lithium and calcium hydrides.

In addition to preparative work with the hydride "amalgams", some exploratory experiments on their thermal stability and behavior toward air and water were carried out. In order to distinguish between formation of a true solution or amalgam on the one hand, and a dispersion on the other, investigations were conducted to determine whether the freezing point of the mercury is depressed. Finally, rough particle-size measurements were made through filtration experiments.

Materials.-- The cerium and lanthanum metals were obtained from Dr. F. H. Spedding, of the Institute for Atomic Research and Atomic Energy Commission Laboratories, in Ames, Iowa. The lanthanum contained up to 500 ppm of cerium, praseodymium, and neodymium. The cerium contained up to 500 ppm lanthanum and neodymium. Each contained roughly 150 ppm calcium, and a few ppm magnesium and iron, as well as some oxide, nitride, and carbide inclusions.

The hydrogen was generated as needed in exceedingly pure form by the thermal decomposition of uranium hydride (14). The mercury employed was

(14) F. H. Spedding, A. S. Newton, J. C. Warf, et al., *Nucleonics*, 4, No. 1,4 (1949).

of analytical reagent grade.

Cerium Hydride "Amalgams". -- A simple apparatus was constructed, consisting of two small bulbs connected through a T to the high vacuum line. One bulb held the cerium, as a single piece of polished metal, and the other the mercury. Hydrogen up to 20-100 mm. was admitted, and the cerium heated using a molten salt bath, first around 150° , and finally at 325° . When

the absorption of hydrogen was complete, the hydrogen pressure was raised to one atmosphere, and the hydride cooled. It had a gray, metallic appearance, not unlike coarsely-powdered graphite. The composition of cerium hydride prepared by this procedure was found to fall between $\text{CeH}_{2.6}$ and $\text{CeH}_{2.8}$. The double-bulb apparatus was evacuated and torched off from the vacuum line.

On rotating to permit the mercury to flow onto the cerium hydride, it was found that slow wetting occurred, several hours passing before no more visible change could be detected. A preparation containing 34 per cent cerium hydride formed a stiff, shiny ball, while a second preparation, 19 per cent cerium hydride, was lustrous and considerably thinner, and adhered to the glass in spots. A thin portion could be poured away from a mass of solid phase wet with mercury. A 5.1 per cent amalgam was similarly heterogeneous, and appeared to change but little on long agitation.

Another cerium hydride sample was agitated violently in a bulb (Fig. 1) by an eccentric drive for 62 hours before addition of the mercury. The shaking process effected a finer subdivision of the powder, and the mercury wet the specimen completely within 30 minutes. This "amalgam", 4.8 per cent hydride, adhered to the glass considerably more than the earlier samples. In another preparation, the cerium hydride was pulverized thoroughly by rapid shaking 43 hours with a glass hammer (Fig. 2), giving a black powder. This material was wet instantly by mercury, forming a viscous, nearly homogeneous "amalgam" 5.5 per cent hydride. No temperature change was noted. It adhered to the glass tenaciously, forming a mirror, and was indistinguishable from uranium hydride "amalgams" in appearance. A few dark specks floated on the surface, evidently oxide and other impurities.

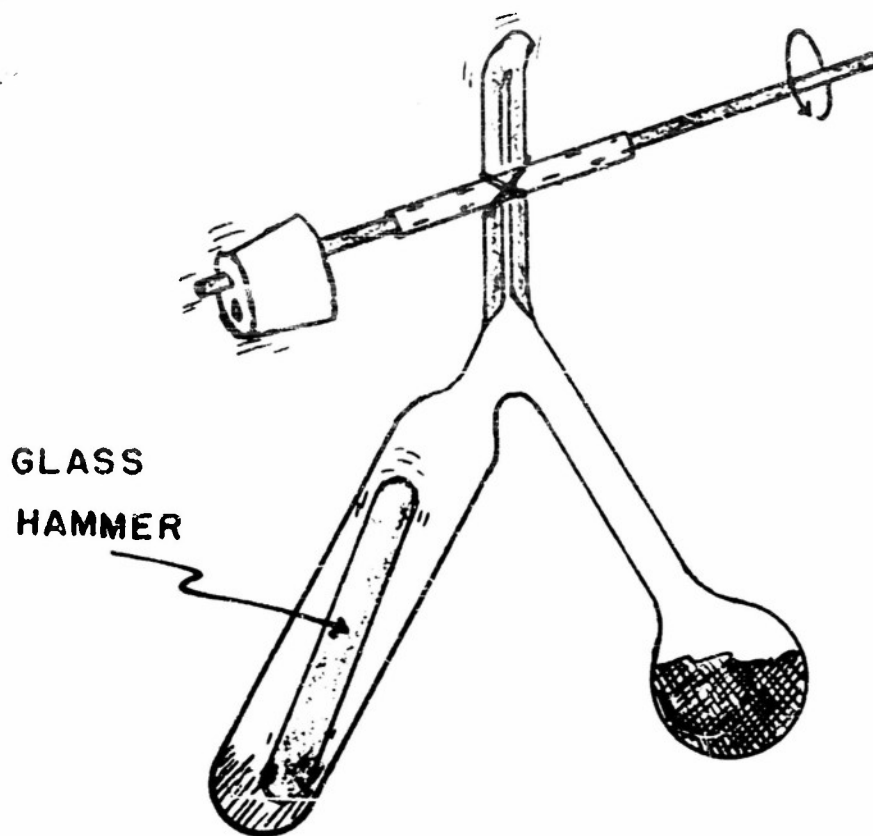
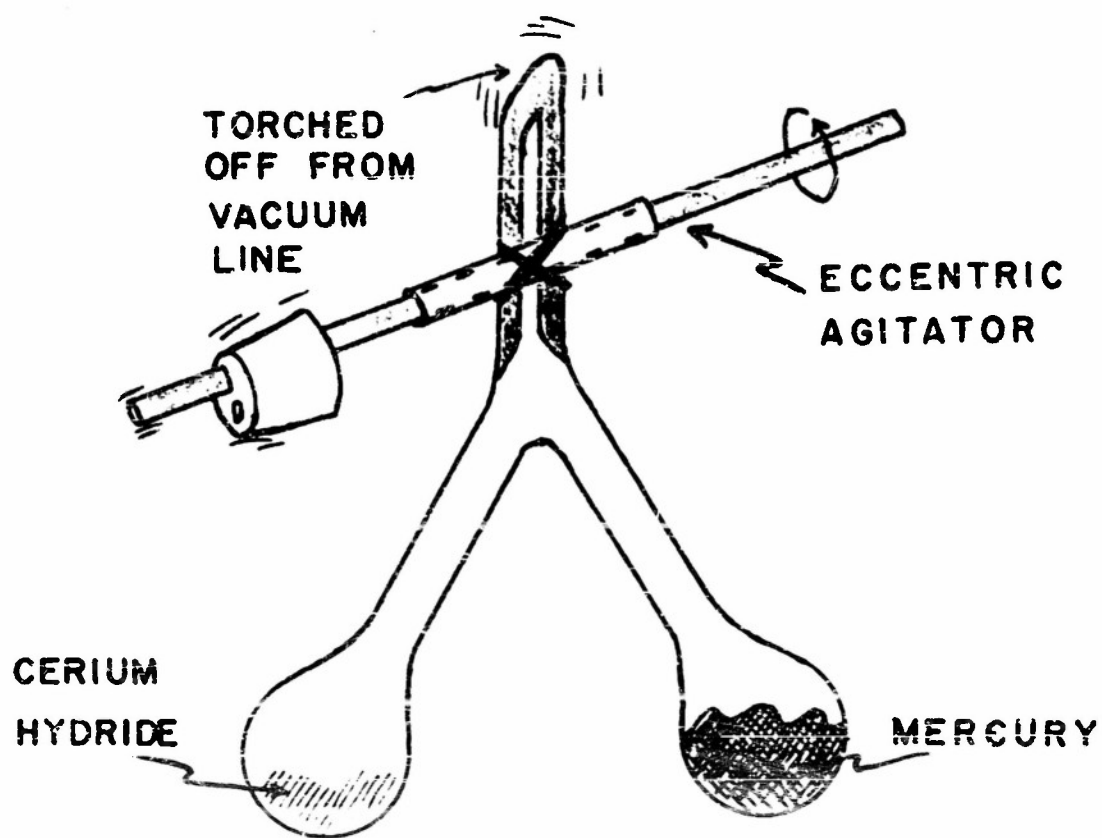
The formation and physical stability of such "amalgams" suggested that they were dispersions, as in the case of uranium hydride dispersions in mercury (12). The difference in density between mercury (13.6 g/cc) and cerium hydride (5.6 g/cc) is considerably greater than in the case of mercury and uranium hydride (10.9 g/cc), a factor apparently unimportant in the dispersion process. The strong adherence to glass, forming mirrors, is evidently due to lowering of the interfacial tension between glass and the mercury by the dispersed hydride.

Figure 1

Apparatus for Preparation of Cerium Hydride,
Agitation, and its Treatment with Mercury

Figure 2

Apparatus for Preparation and Pulverization of
Cerium Hydride, and its Treatment with Mercury



Lanthanum Hydride Amalgams. -- Lanthanum hydride approaching LaH_3 in composition was prepared and pulverized as with cerium hydride (Fig. 2). It was wet avidly by the mercury, forming a stiff dispersion, 16.8 per cent lanthanum hydride. The "amalgam" adhered strongly to the glass, forming a mirror.

Thermal Stability of Cerium Hydride "Amalgam" -- A 5.1 per cent cerium hydride "amalgam" attached to the vacuum system was heated in a bath. It was found that the first noticeable hydrogen was evolved at $115-120^\circ$, and that at 200° hydrogen was being expelled extremely rapidly. Mercury-cerium intermetallic compounds are evidently formed. The stability of the "amalgams" at room temperature on long storage is not yet known with certainty.

It is evident that all metal hydrides decompose on heating with mercury, forming hydrogen and true amalgams. This includes such diverse substances as LiH , $\text{PdH}_{0.6}$, UH_3 , and $\text{CeH}_{2.7}$.

Reaction of Cerium Hydride "Amalgams" with Air and Water. -- During the course of the "amalgam" work a number of dispersions were exposed to the air. Concentrated mixtures of cerium hydride and mercury, on admission of air, rapidly developed voluminous black precipitates, and invariably ignited spontaneously within a few minutes. A portion of the black precipitate was rapidly withdrawn before ignition, and sealed in a capillary. Its X-ray diffraction pattern showed it to be reasonably pure cerium hydride. It would appear as if formation of an oxide layer on the hydride particles resulted in the separation of the particles from the mercury, disrupting the dispersion. The behavior of uranium hydride dispersions is parallel.

On admission of air to the more dilute "amalgams", a thin layer of yellowish-green scum formed over the shiny surface. A portion of this scum, by X-ray analysis, was identified as cerium dioxide of poor crystallinity or small particle size (diffuse lines). Ignition of the yellowish material gave a white product, which corresponded to highly crystalline cerium dioxide (sharp diffraction lines). Some of the dilute cerium hydride "amalgams" after forming the yellowish scum (accompanied by a uniform increase in weight on standing), later deposited the dark hydride, and eventually ignited (with a discontinuous increase in weight).

One bulb of cerium hydride "amalgam" (4.8 per cent) was broken under water. A vigorous reaction ensued, with abundant evolution of hydrogen, and with considerable sparking. It should be noted that uranium hydride "amalgam" is relatively inert toward water (12)/

Freezing and Melting Curves of Hydride "Amalgams". -- While previous work had suggested that cerium hydride "amalgams" were not true solutions, but dispersions, it was still conceivable that a small fraction dissolved to form a genuine amalgam. The rather high molal freezing point depression constant of mercury [39.4° , based on a heat of fusion of 2.34 kilojoules per g-atom (15)] affords a sensitive means of testing this point by

(15) Int. Crit. Tab., II, 458 (1927).

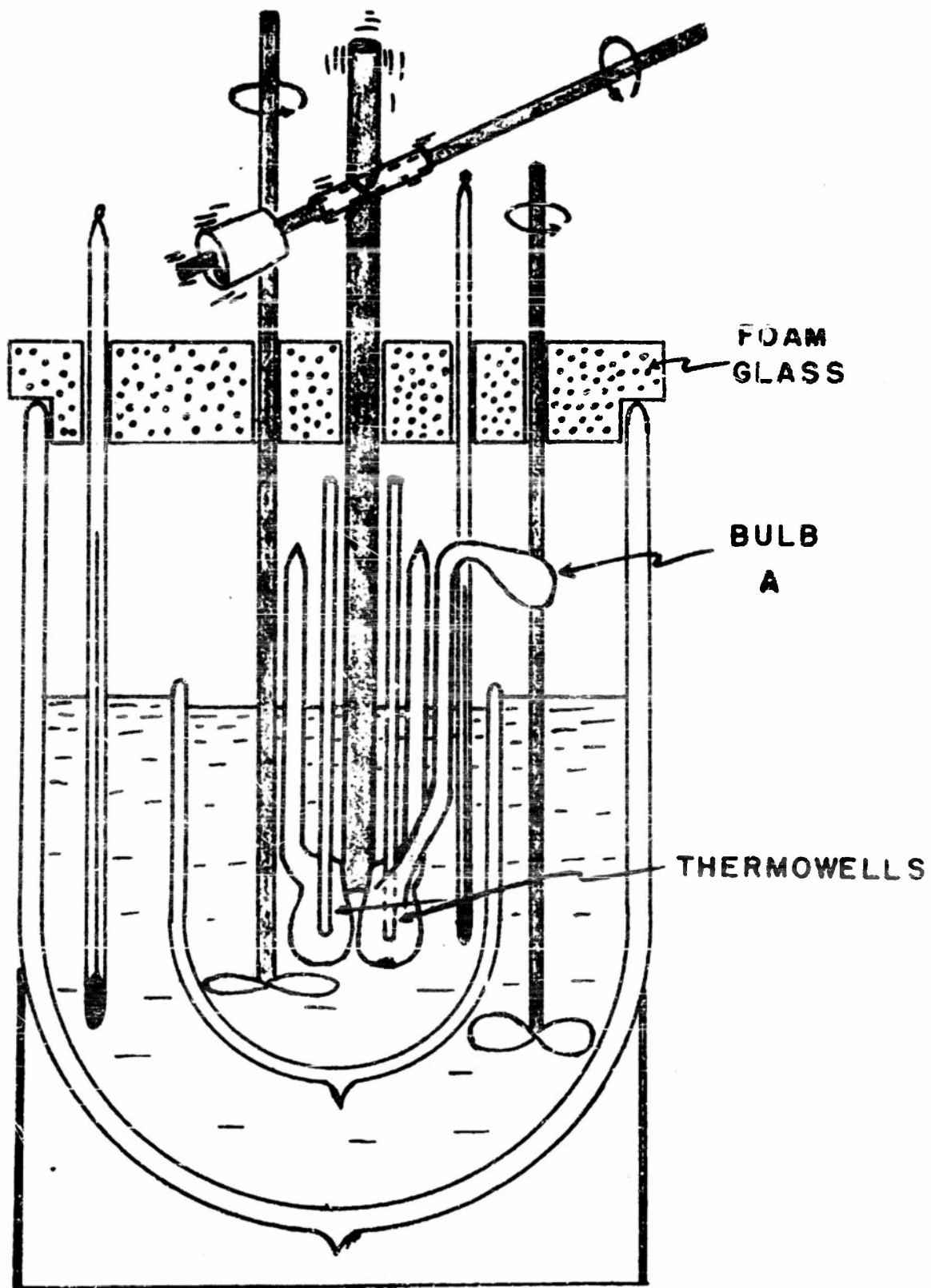
detecting any freezing point depression.

a) Apparatus and Procedure. A melting and freezing apparatus for work in the neighborhood of -40° was assembled (Fig. 3). This consisted of two thin-glass bulbs of approximately 3 ml. capacity, each with a thermowell in its center, both bulbs being supported by a rod attached to an eccentric shaking device. The adjacent bulbs were immersed in a dry ice-trichloroethylene mixture, contained in a 300 ml Dewar, which in turn was immersed in a 4-liter Dewar filled with the same freezing mixture. Both baths were stirred mechanically, and equipped with alcohol thermometers. The large Dewar was covered with a sheet of 2-inch foam-glass insulation.

The double-Dewar assembly was employed only in the freezing runs, when the larger vessel was chilled to approximately -70° . This caused the contents of the inner Dewar, at about -37° , to drop in temperature at a rate of about 0.05° per minute. For melting runs the inner Dewar was removed, when thermal leakage caused the temperature, about -40° , to rise at a rate of roughly 0.06° per minute.

As the scale of operation was too small to permit use of resistance thermometers, temperatures were measured using copper-constantan thermocouples or 3-element thermopiles. These were generally employed with the reference junction at 0° in a water-crushed ice mixture, one of the bulbs being empty. In certain runs the thermocouple or thermopile was used to measure the temperature differential between the two bulbs. The differential method provided data ambiguous in interpretation (except when both bulbs contained pure mercury) and was discontinued.

Figure 3
Apparatus for Freezing and Melting Runs
With Hydride "Amalgams"



The potentiometer used was a Model 8662 Leeds and Northrup Precision Potentiometer. Its precision was 0.002 mv. (0.06°) with the thermocouples, or 0.00067 mv. (0.02°) with the 3-element thermopile. Temperature-emf data were taken from the tables of Adams (16).

(16) L. H. Adams, *Int. Crit. Tab.*, I, 58 (1926).

b) Results

1. Mercury. Melting and freezing curves using pure mercury were first obtained (Figs. 4 and 5). The freezing curves show strong supercooling despite the violent agitation. The plateaus were at $-38.84^\circ \pm 0.03^\circ$, in satisfactory agreement with the very accurate value of -38.87° , determined by Smits and Müller (17).

(17) A. Smits and G. S. Müller, *Z. physik. chem.*, B36, 288 (1937).

2. Uranium Hydride "Amalgam". A 30.3% uranium hydride "amalgam" was prepared by sealing the uranium in bulb A (Fig. 3), converting it to UH_3 by heating in hydrogen at 250° , evacuating and sealing off the apparatus, and tapping the hydride down onto the mercury in the freezing point bulb. This gave a fairly viscous preparation which adhered strongly to the glass.

Melting and freezing curves for the uranium hydride "amalgam" are shown in Figs. 6-8. The plateaus, at $-38.86^\circ \pm 0.03^\circ$, were within experimental error of the melting point of pure mercury. The principal difference was found in a tendency to exhibit a prolonged post-melting period at a temperature roughly a tenth of a degree above the melting point (Fig. 8). This effect was nearly eliminated by more violent agitation (Fig. 7), and was not manifest in freezing runs (Fig. 6), evidently being masked by the supercooling. The post-melting phenomenon is probably attributable to the viscous nature of the hydride dispersion.

3. Cerium Hydride "Amalgam". A 5.1 per cent cerium hydride dispersion in mercury was made by the technique described above, and melting curves obtained (Fig. 9). The plateaus, at $-38.83^\circ \pm 0.03^\circ$, were substantially the same as in the previous cases. The prolonged post-melting period, with the temperature a little above the melting point, was again prominent, and was ascribed to the higher viscosity of the "amalgam."

c) Discussion. A typical cooling or freezing curve for a very dilute, true solution, in which crystals of the pure solvent separate, is shown in Fig. 10 (lower curve) (18). After the initial supercooling,

(18) C. R. Witschonke, Anal. Chem., 24, 350 (1952).

the temperature rises, but does not reach the true melting point, which is shown by the plateau of the pure solvent (upper curve). Extrapolation of each curve backwards normally gives the initial depression of the freezing point of the solution, a depression which increases with time, as the solution becomes more enriched in the solute, owing to crystallization of the solvent. The freezing point (A) and melting point (B) of the solution are clearly different.

The fact that the temperature of the uranium hydride "amalgam", after the end of the supercooling period, rose to substantially the freezing point of the solvent (Fig. 6) demonstrates that no depression of the freezing point took place. The cerium hydride "amalgam" also exhibited supercooling, and the temperature rose to the freezing point of pure mercury. Moreover, the initial part of the plateau of the melting curves in each case coincided within experimental error with the solvent melting point (Fig. 7), in a region where the depression would have been maximum had there been genuine solution formation.

The lack of a freezing point depression corroborates the conclusion that the "amalgams" are in reality dispersions, and the disposition of the mercury can be likened to that of water in a sponge. The dispersions probably borderline the colloidal state. Assuming a sensitivity limit of 0.03° in the temperature-measuring apparatus, and thus a maximum freezing point depression of 0.03° , the true solubility of the hydrides in mercury could not have been over 0.0007 molal, corresponding, in the case of cerium hydride, to 0.1 g per 1000 g. of Hg, or 0.01 per cent.

Filtration of Cerium Hydride Amalgams. Particle Size. -- Two cerium hydride "amalgams" were decanted or filtered in an all-glass apparatus, and the filtrates analyzed. The first specimen of cerium hydride, treated with mercury without any prior powdering or agitation, was decanted through a constriction so that the fluid portion could be collected separately. The apparatus was broken and the fluid portion analyzed for cerium, showing

Figure 4

Freezing Curve for Pure Mercury

Figure 5

Melting Curve for Pure Mercury

Figure 6

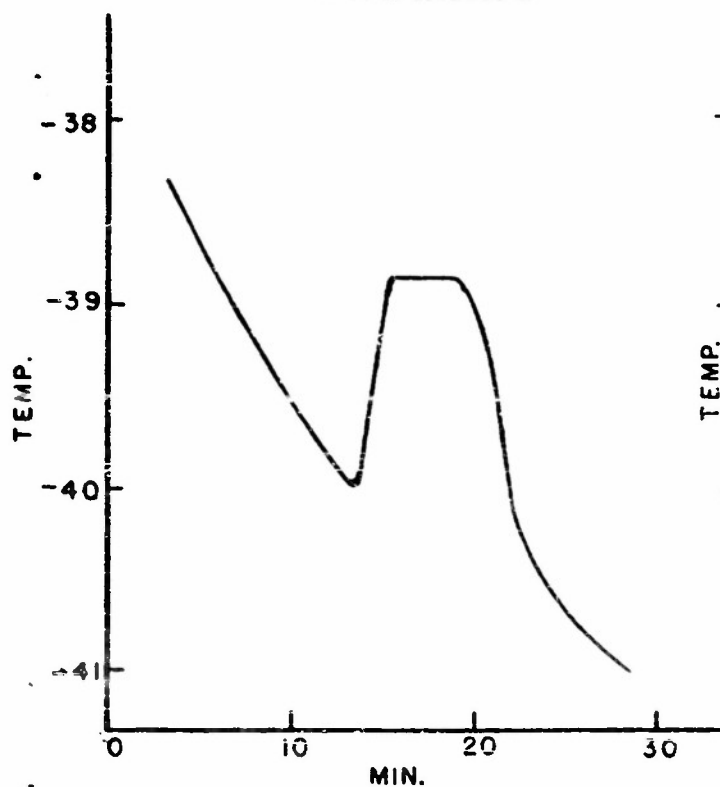
Freezing Curve for Uranium
Hydride Dispersion in Mercury

Figure 7

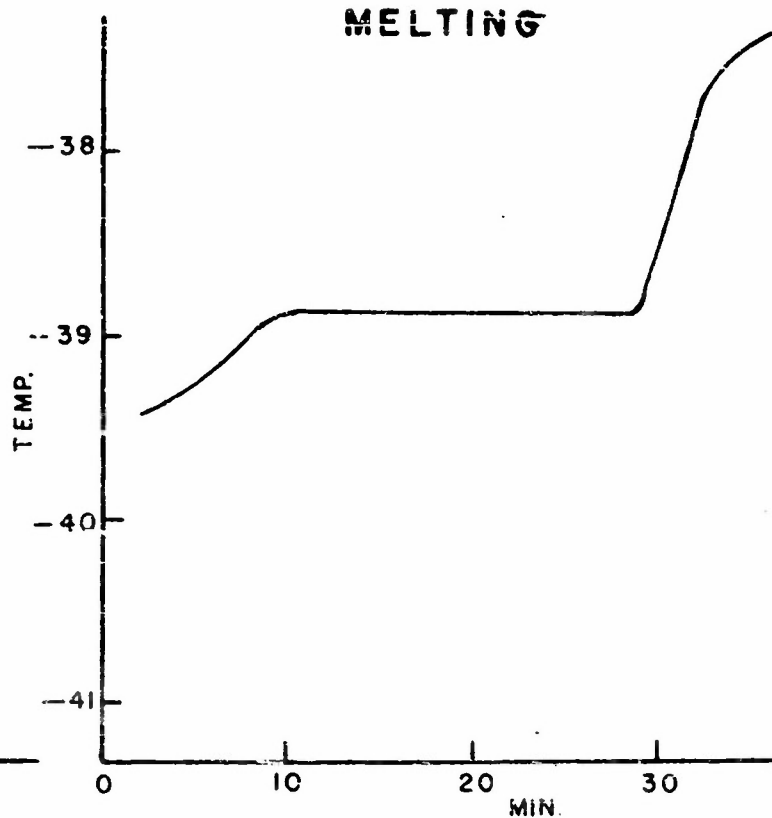
Melting Curve for Uranium
Hydride Dispersion in Mercury

PURE MERCURY

FREEZING

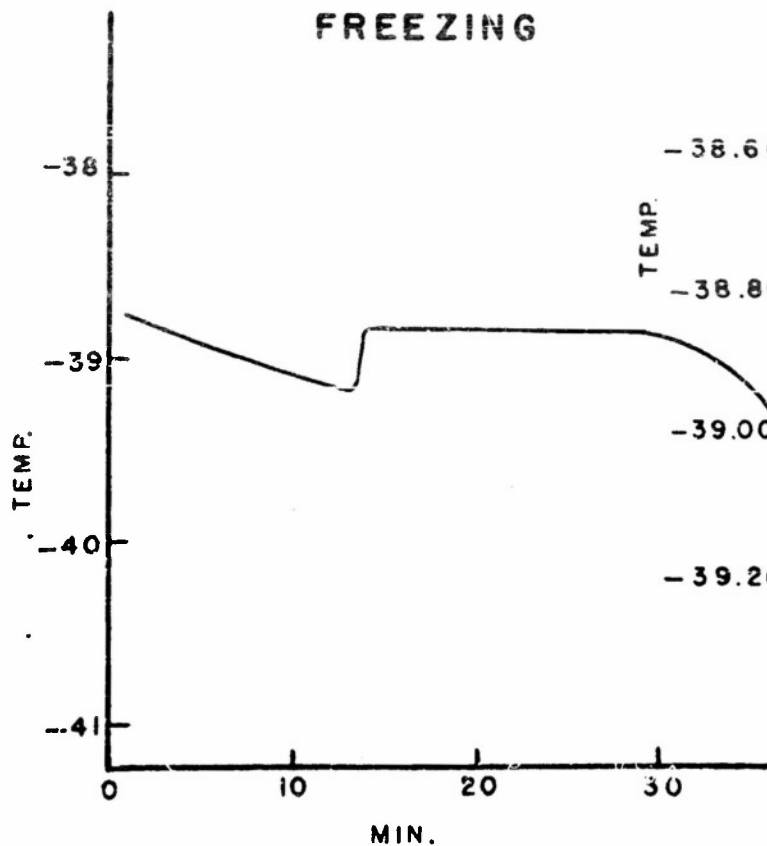


MELTING



URANIUM HYDRIDE AMALGAM

FREEZING



MELTING

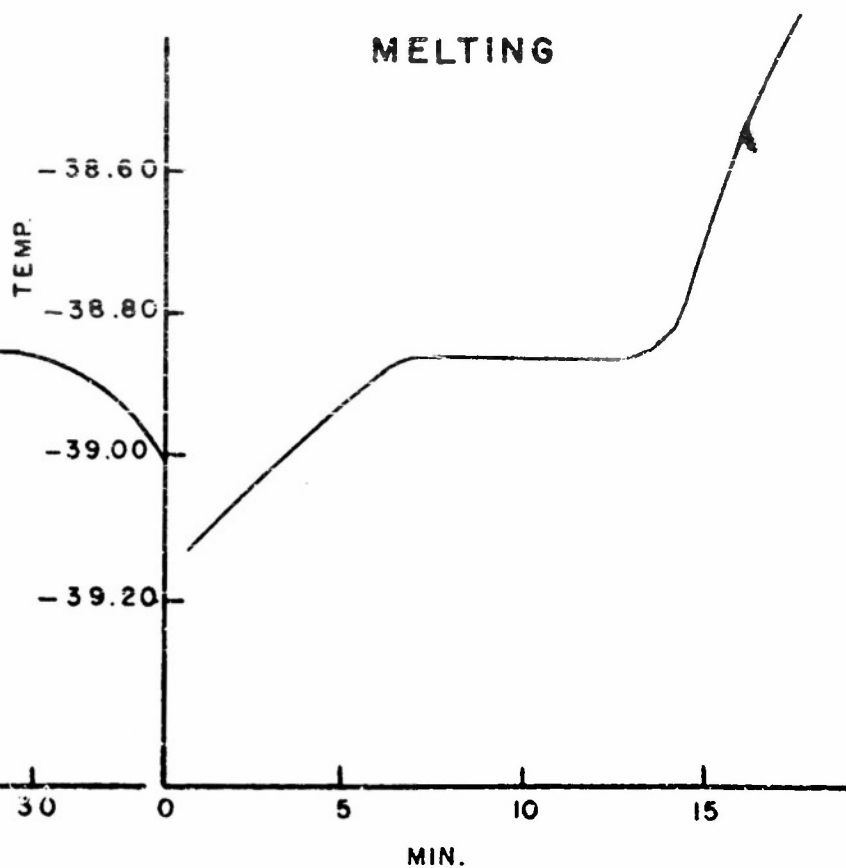


Figure 8

Melting Curve for Uranium
Hydride Dispersion in Mercury

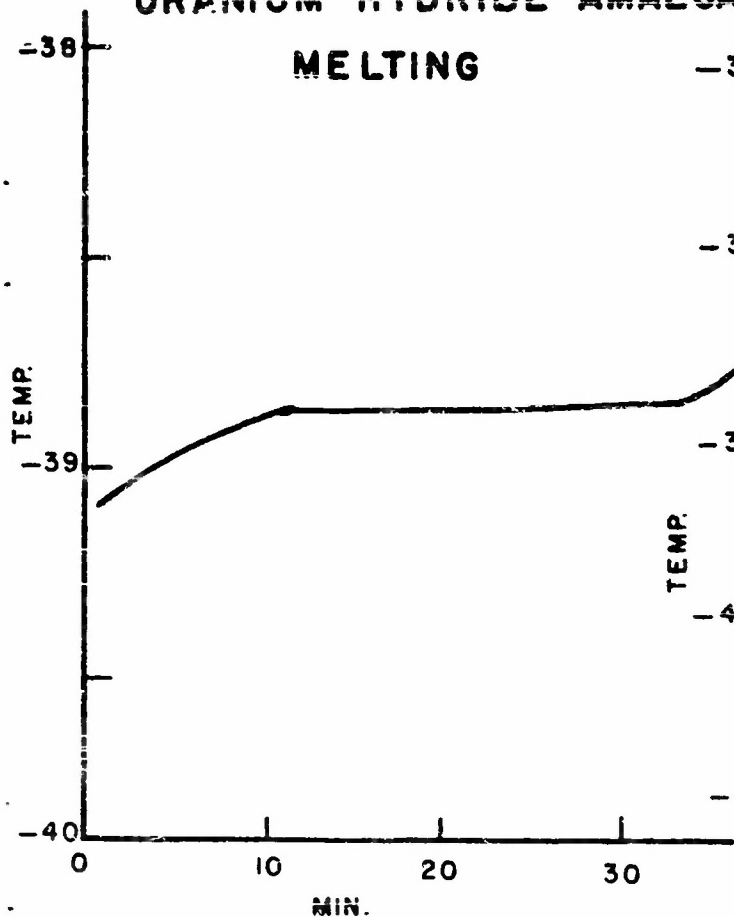
Figure 9

Melting Curve for Cerium
Hydride Dispersion in Mercury

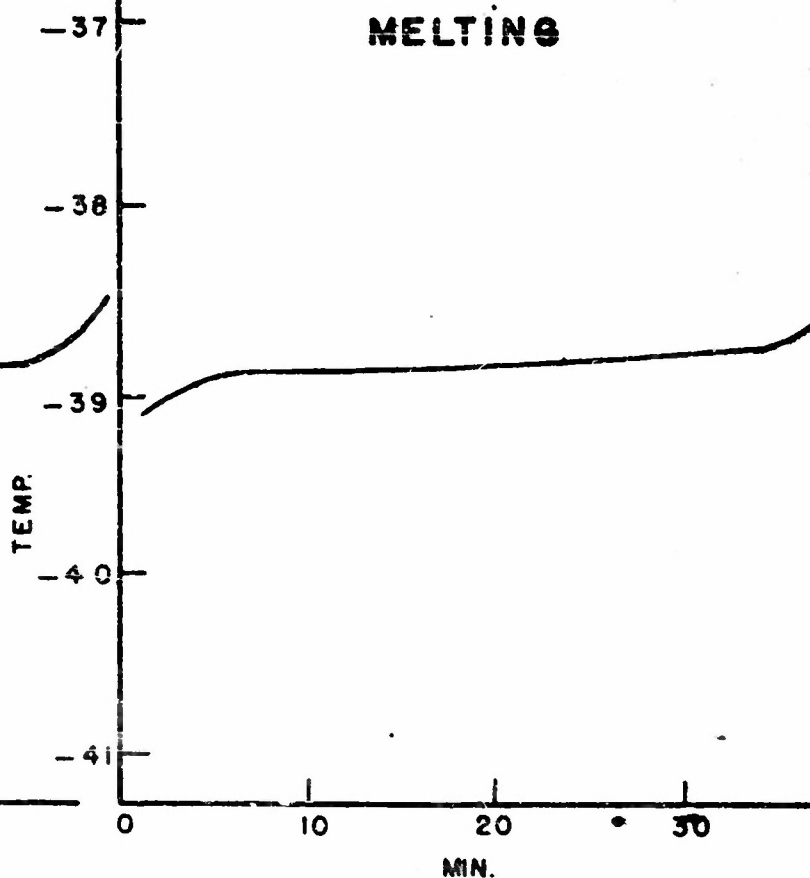
Figure 10

Freezing Curves for a Pure Solvent and a Solution

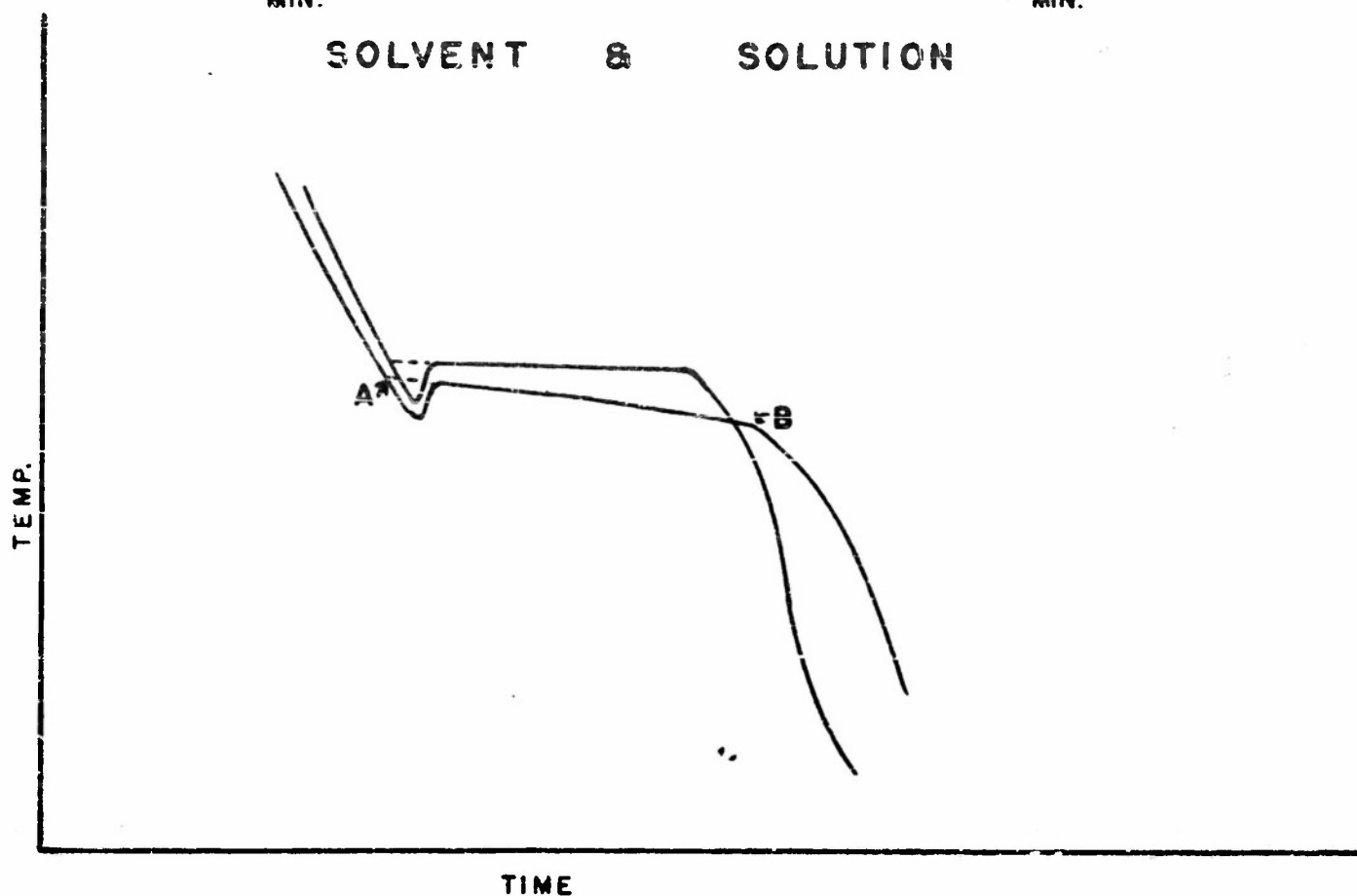
URANIUM HYDRIDE AMALGAM MELTING



CERIUM HYDRIDE AMALGAM MELTING



SOLVENT & SOLUTION



0.085 per cent cerium hydride. The overall composition prior to decantation was 4.3 per cent cerium hydride. It is thus evident that when cerium is converted to its hydride, a wide range of particle sizes results; the larger particles form a compact mass when "moistened" with mercury, and the smaller particles enter into dispersion in the mercury.

A second portion of cerium hydride was prepared and pulverized by the eccentric drive-hammer technique (Fig. 11), and amalgamated. The powdering treatment was for a duration of 43 hours before addition of the mercury and 5 hours afterward. The stiff dispersion, 5.5 per cent cerium hydride, was shaken down into the sidearm with a fine sintered glass filtering disk. This sidearm was torched off and centrifuged, when a thick, nearly solid residue was left on the disk, representing a concentrated "amalgam", and the filtrate had the appearance of pure mercury. The filtrate was found by analysis to contain 0.0079 percent cerium hydride. The average maximum pore size of "fine" sintered glass is approximately 5μ . It is probable that only a small fraction of the finely pulverized cerium hydride is smaller than 5μ in particle size.

The maximum true solubility of cerium hydride in mercury at its freezing point was shown to be 0.01 per cent. The above filtration experiment demonstrates a value somewhat lower, at room temperature, namely approximately 0.008 per cent.

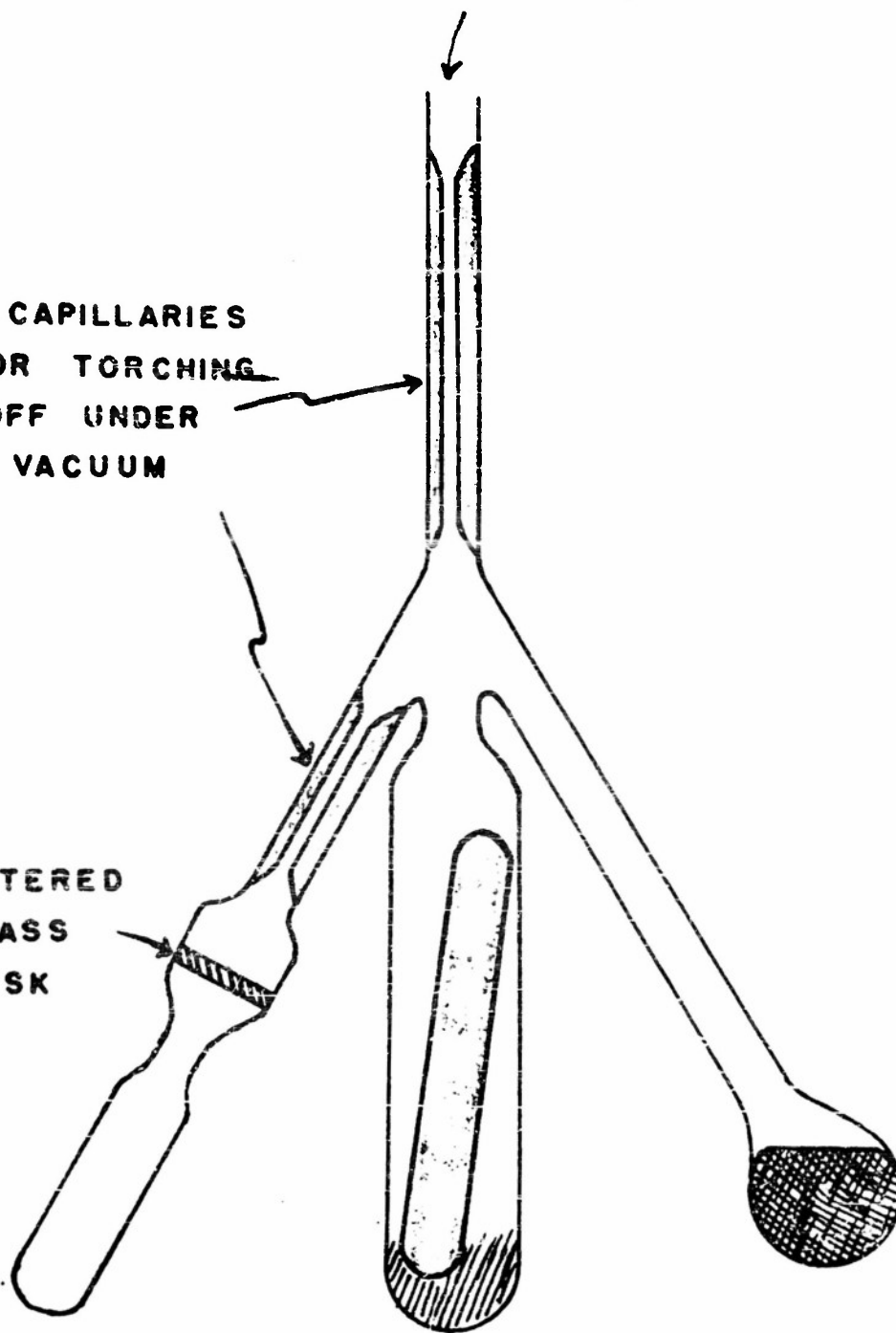
Figure 11

**Apparatus for Preparation, Pulverization, "Amalgamation",
and Filtration of Cerium Hydride**

TO VACUUM LINE

CAPILLARIES
FOR TORCHING
OFF UNDER
VACUUM

SINTERED
GLASS
DISK



II. RARE EARTH METAL-HYDROGEN SYSTEMS

Introduction

The following short sections are intended to serve as a progress bulletin on the status of studies of the rare earth hydrides. More complete reports on these and other investigations will appear in the future. High pressure and conductimetric work is underway or planned for the immediate future, and preparation of borohydrides, reaction of hydrogen with rare-earth alloys, and magnetic susceptibility measurements are to follow.

A. Dissociation Pressure Studies.

First attempts employed a Pyrex reaction vessel heated by a mercury boiler, such as had been used in studying the dissociation of uranium hydride (14). It was found, however, that a temperature of 357° was insufficient to give adequate data, since the dissociation pressure for cerium hydride decreased to a value of less than 10 mm. of mercury at a composition approximating $CeH_{2.2}$ and an extrapolation of the pressure-composition curve for this temperature indicated that this dissociation pressure decreased to 1 mm. Hg at a composition well above CeH_2 . Lanthanum hydride behaved similarly. The cerium and lanthanum hydrides richest in hydrogen that were obtained had the compositions $CeH_{2.87}$ and $LaH_{2.96}$.

Vycor reaction vessels, heated by a resistance furnace, were used at higher temperatures, but reaction between the rare-earth metal and the vessel was found to occur at temperatures of about 800° . Stainless steel thimbles were also found to react slightly with the rare-earth metals at these temperatures.

One sample of lanthanum hydride was heated to 900° in Vycor and a composition $LaH_{1.57}$ reached by pumping the hydrogen evolved into a gasburet by means of a Toepler pump. The Vycor was seriously attacked.

The relatively low dissociation pressures of the hydrides compared with, say, uranium hydride, prompted the construction of a thermostatted high-temperature furnace, described in Section B of this report. Dissociation pressure studies are planned for the rare earths La, Ce, Pr, Nd, Sm, and Yb, using the high-temperature furnace and torsion balance (Part C).

B. High-Temperature Thermostatted Furnace.

A temperature-controlled laboratory furnace similar to that described by Barnes (19) was constructed. A cross-sectional diagram of the furnace

(19) R. S. Barnes, J. Sci. Instr. 28, 89 (1951).

itself is shown in Figure 12, and a circuit diagram of the temperature controller in Figure 13. A fuller theoretical discussion than the following may be found in the original paper.

The furnace contained two independent sets of heating elements. The first of these, wound on an Alumina core, had a resistance of 10.5 ohms, and consisted of No. 15 nickel-chromium wire. This winding was used as an aid in bringing the furnace more quickly to the desired temperature. The second heating element was the control winding itself, comprising R_1 and R_2 in the control circuit, c' platinum and nickel-chromium wires, respectively.

The heat provided by the control winding alone was sufficient to maintain the furnace at temperatures in excess of 800° . The platinum and nickel-chromium wires were threaded side-by-side through a series of twin-bore porcelain thermocouple insulators, forming a mat which was wrapped around an Inconel block, the whole then being enclosed in an Inconel sheet.

The resistances R_1 and R_2 form part of a bridge circuit, the balance point of which changes with temperature, as the two wires possess widely differing temperature coefficients of resistance.

A small Variac-type transformer (T_2) was used for the other arms of the bridge. The out-of-balance voltage from the bridge was amplified by the audio-frequency transformer (T_3) with a series resonant circuit (L_1 and C_1) tuned to 60 c/s connected across the secondary winding. The amplified out-of-balance voltage was applied to the grid of V_1 , a small thyatron with an alternating current applied to its anode. The voltage from the bridge undergoes a phase reversal at the balance point, and the phase of the anode voltage was arranged so that V_1 conducts during the positive half cycles if the temperature is below the balance temperature and does not conduct if the temperature is above.

When V_1 is conducting, the anode current closed a thermal delay relay tube V_2 , which short circuited the resistor R_3 in series with the bridge, causing the heating element to heat up. When the temperature has risen

Figure 12
High-Temperature Thermostatted Furnace
(after Barnes)

Leads to core

Leads to block

Plug

Plug

Vermiculite
Insulation

Spiral Grooved
Alundum Core

Coiled Heating
Element

Quills containing
heating element

Inconel sheet

Inconel block
Heavy ribbon element

Shell No. 16 Gd.
Sheet Iron

Angle-iron support

4" Dia.

18"

L.W. Firecrete

15" Dia.

FURNACE

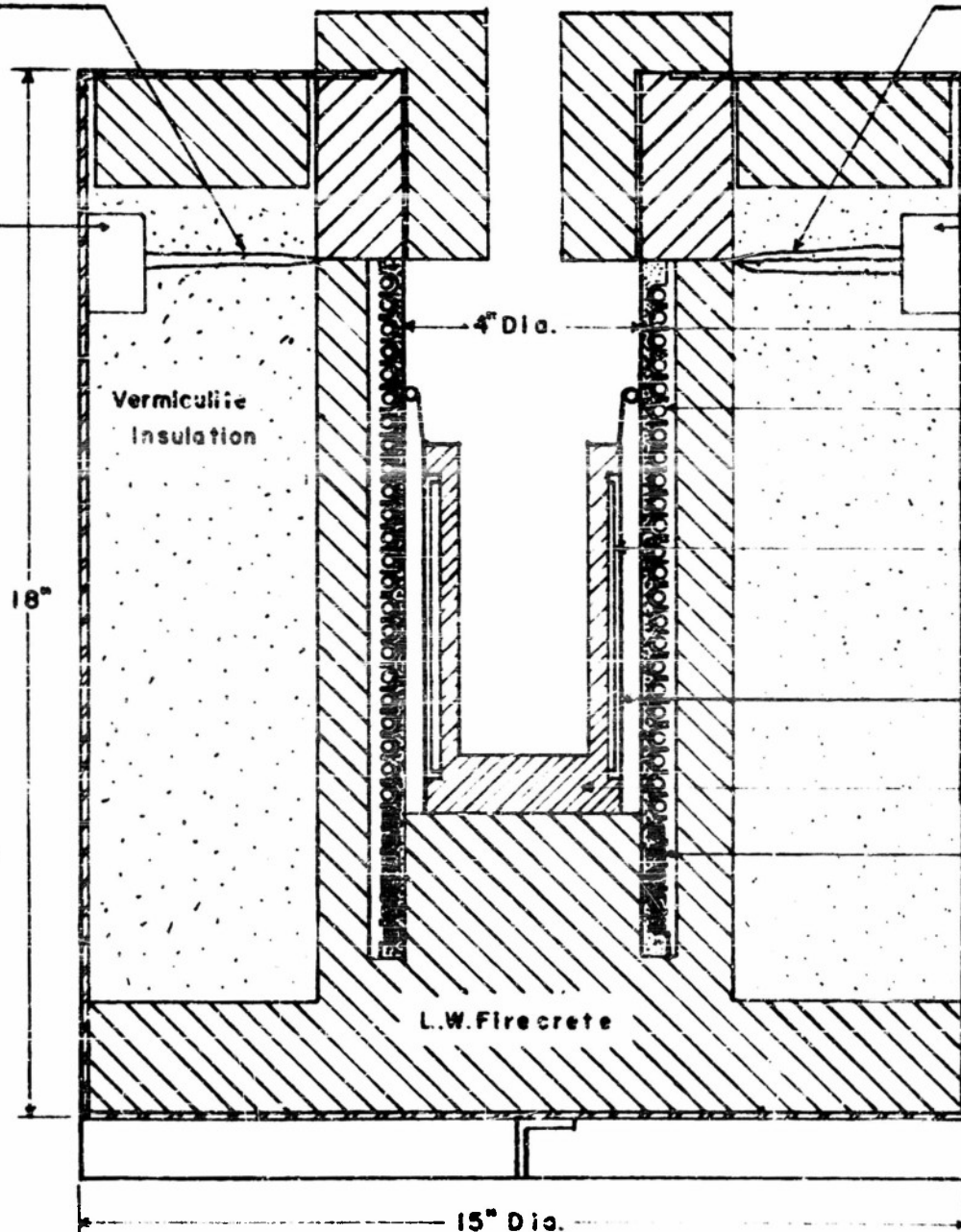
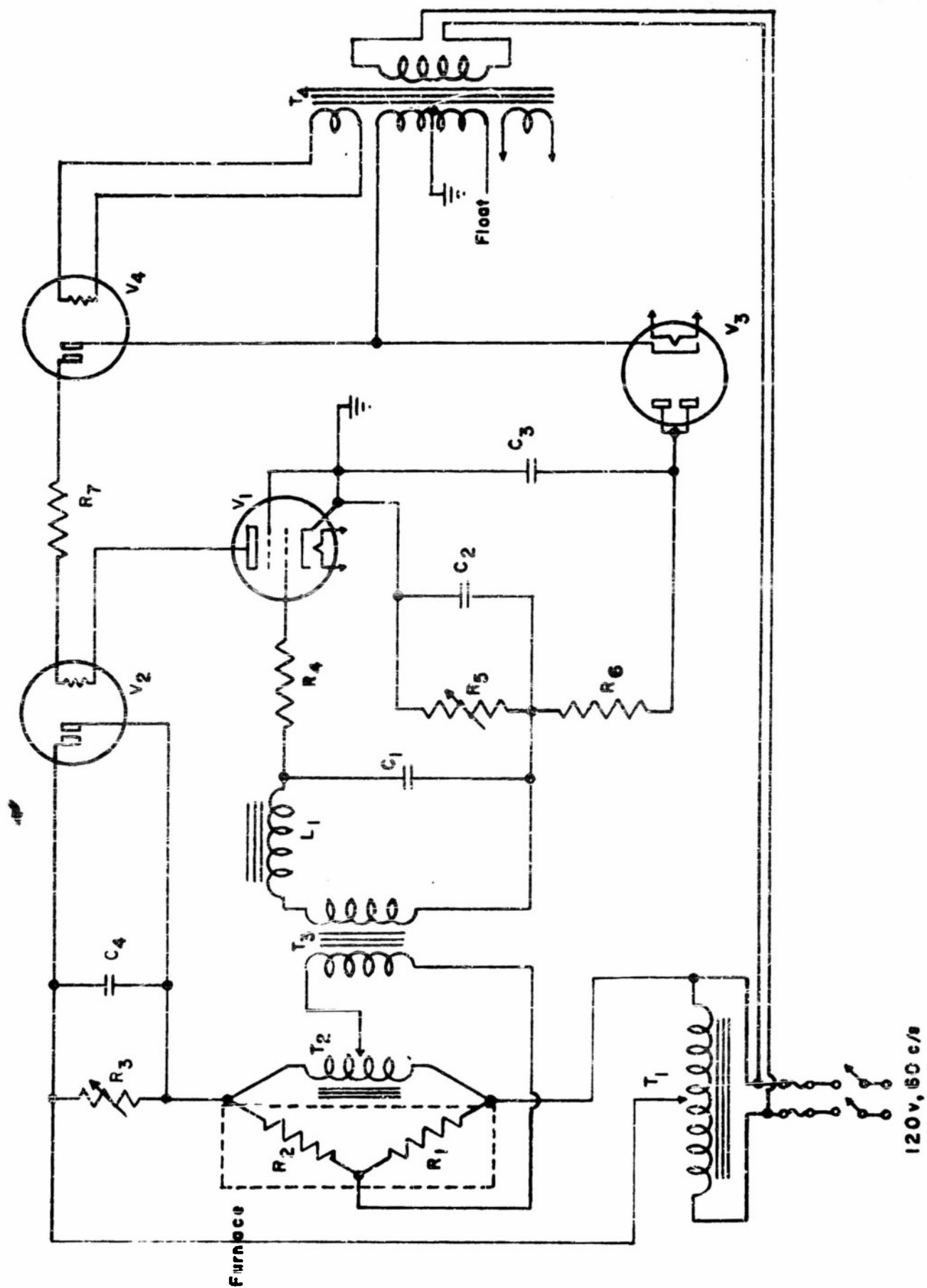


Figure 13

Circuit Diagram for Automatic Temperature Controller
(after Barnes)

List of Components

- R_1 - 5 ohm, No. 26 platinum wire.
- R_2 - 12 ohm, No. 20 Chromel A wire.
- R_3 - 25 ohm, 300 W.
- R_4 - 1 Mohm, 1 W.
- R_5 - 50 kohm, 7 W., wire-wound.
- R_6 - 300 kohm.
- R_7 - 10 kohm, 10 W.
- C_1 - 0.30 μ F.
- C_2 - 16 μ F.
- C_3 - 2 μ F.
- C_4 - 0.25 μ F.
- L_1 - 9 H, 150 mA.
- T_1 - Variac, 10 A, 135 v.
- T_2 - Variac, 1 A, 135 v.
- T_3 - Audio Transformer, impedance ratio primary to secondary: 4000.
- T_4 - 117 v, 60 c/s; 600 v, 75 mA; 5 v, 2 A; 6.3 v, 3 A.
- V_1 - 2050.
- V_2 - Amperite Thermostatic Delay Relay 115NO5.
- V_3 - 6X5-GT.
- V_4 - Amperite Thermostatic Delay Relay 5NO45.



sufficiently, V_1 no longer conducts, as the phase of the out-of-balance voltage is reversed. The switching frequency of V_2 can be much higher than is normally the case, as its heater remains hot. Barnes reported the frequency of switching as about 2 c/s.

However, this high a frequency was not obtained with the controller built as described; a complete switching cycle occurred only about every 3-1/2 sec. Substitution of a solenoid relay, in parallel with a suitable capacitance and in series with a suitable resistance, replacing R_7 , gave a frequency of switching as high as 2 c/s.

The change in temperature of the furnace was only about 0.2° at 718° over a 26-hour period, as measured with a Chromel-Alumel thermocouple and the potentiometer described on p!4 .

C. Silica Torsion Balance.

In order to determine conveniently the composition of the solid phase in the rare earth-hydrogen system studies, a micro torsion balance was constructed, and assembled inside the vacuum system. Except for a steel spring, the entire balance was fabricated from silica. The design selected was a modification of that of Kirk et al. (20).

(20) P. L. Kirk, R. Craig, J. E. Gullberg, and R. Q. Boyer, Anal. Chem., 19, 427 (1947).

The general assembly is shown in Figure 14. The torsion fiber was 13 cm. long on the fore (scale) side of the beam, and 8 cm. long on the rear (spring) side. Its approximate mean diameter was 130μ . The cantilever beam was 16.7 cm. long, and constructed from fairly heavy silica rod (370/11). Tension was applied through the spring by the screw arrangement shown, the whole being enclosed in the vacuum system. The torsion was applied through a ground joint. The balance point was observed by matching the pointed tip of the beam against a fixed pointer, the observation being made against an illuminated ground glass (not shown).

The balance was found to be quite rugged, and the fiber held a total weight (beam, counterbalance, suspension fiber, pan, and specimen) of two grams. The degree of sagging was adjusted by the tension applied to the spring, and was always sufficient to prevent any part of the balance from touching the glass walls of the vacuum system.

The sensitivity of the balance was found to be approximately 7 degrees per milligram. The rest point of the loaded balance was observed to vary slightly from day to day, the average variation being $\pm 1.5^\circ$, or an apparent weight change of ± 0.2 mg. Thus with a load of 850 mg. of lanthanum holding up to 18 mg. of hydrogen (or 36 mg. of deuterium), the weighing error is expected to be ± 0.2 mg. The complete assembly with the Barnes furnace is shown schematically in Figure 15. Pans of various metal foils are being investigated, such as stainless steel, nickel, and molybdenum. It is believed that this apparatus will be satisfactory in the determination of pressure-composition isotherms in the range 600-1000°.

D. Status of X-ray diffraction work.

X-ray powder diffraction photographs have been made of lanthanum and cerium hydrides of various compositions. These products were prepared in an apparatus equipped with a hammer for pulverizing the solid, and to which were attached thin-walled Pyrex capillaries into which the hydride samples were shaken, without having been exposed to the air. The compositions were determined from measurements of the amounts of hydrogen originally absorbed by the metal, and subsequently evolved upon heating.

Diffraction photographs were obtained for lanthanum hydride samples ranging in composition from $\text{LaH}_{1.57}$ to $\text{LaH}_{2.46}$ and for cerium hydride samples from CeH_2 to $\text{CeH}_{2.8}$. Both copper and molybdenum radiation have been used. Copper radiation gave films with high background due to scattering, but having lines in the back-diffraction region, while molybdenum radiation gave films with a much lower background, an advantage offset to some extent by the absence of lines in the back-diffraction region.

All hydride samples gave diffraction patterns corresponding to face-centered cubic lattices considerably expanded over that of the face-centered metallic modification. The lattice spacings were found to be smaller for the hydrogen-rich samples than for those samples containing less hydrogen. Future work will center around the low hydrogen regions, and the hydrides of neodymium, praseodymium, samarium, and ytterbium.

Acknowledgement. -- The authors wish to express their appreciation to the Office of Naval Research for making these investigations possible, and to the Atomic Energy Commission for a Fellowship to one of us (W.L.K.).

Figure 14
Silica Torsion Balance

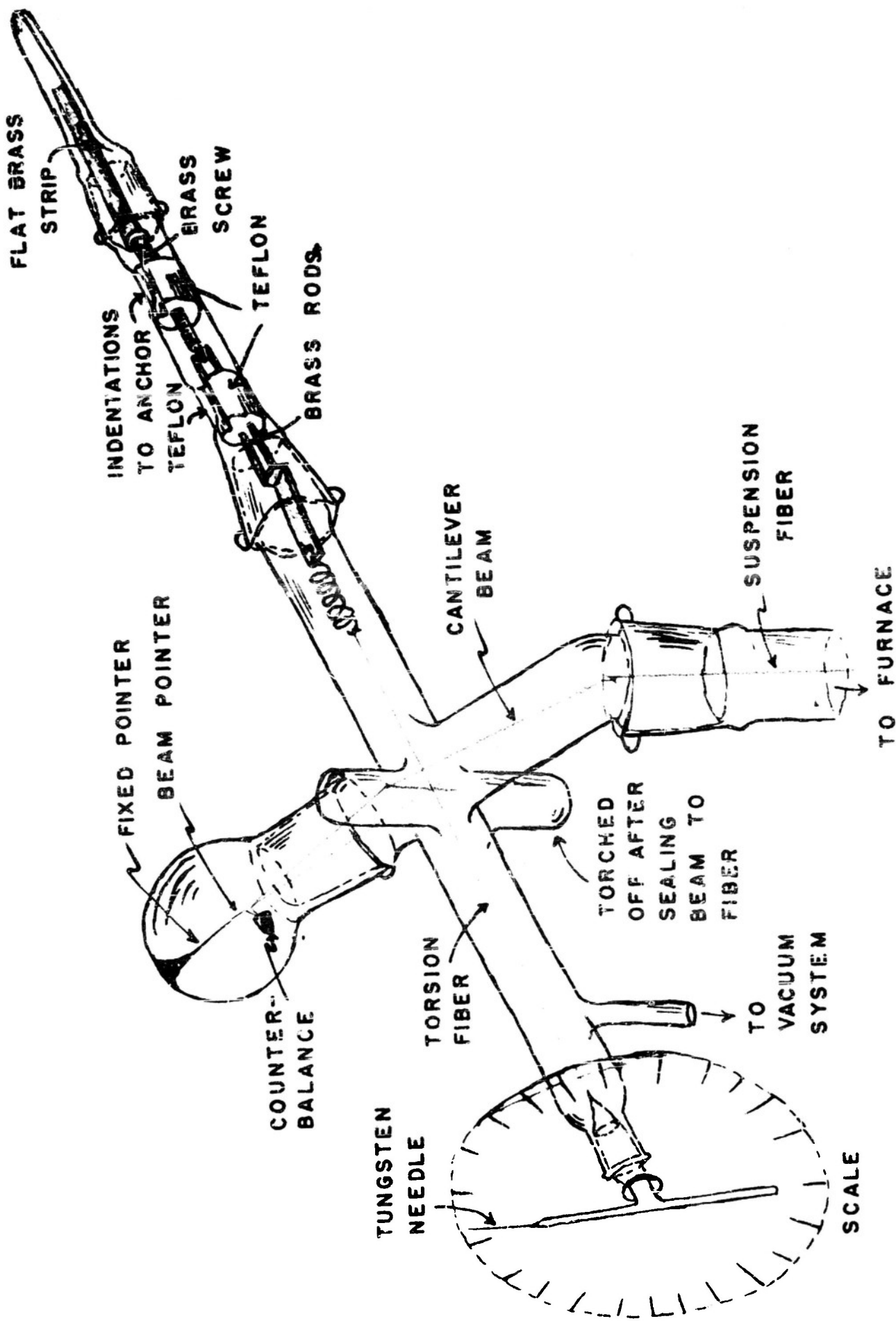
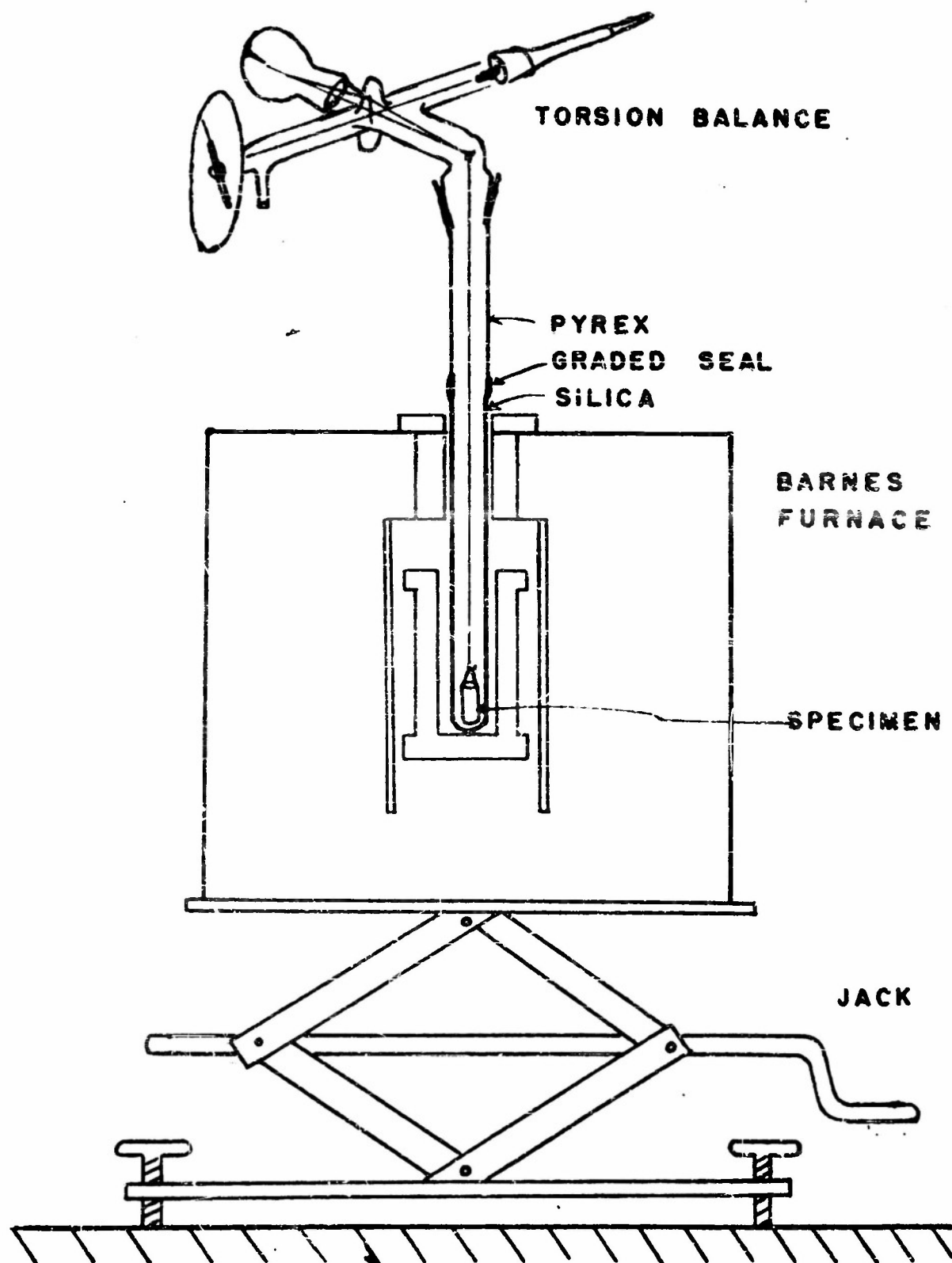


Figure 15
Torsion Balance and Furnace Assembly
(Schematic)



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