ABSORPTION AND DIFFUSION OF HYDROGEN IN THORIUM

by

Donald Gilbert Westlake

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Metallurgy

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State College

Ames, Iowa

1959

TABLE OF CONTENTS

I. INTRODUCTION

Reactor metallurgists are interested in thorium because it produces U_{233} by neutron capture. The efficiency of hydrogen in moderating neutrons has led to an intense interest in metal hydrides, including thorium dihydride. If the thorium-hydrogen system up to the composition of thorium dihydride follows the laws of thermodynamics, its behavior should be specified at equilibrium by the thermodynamic properties, and if surface reaction rates are not controlling, the kinetics of the thorium-hydrogen system should be governed by the rate of diffusion of hydrogen in the phases which are present, namely the gas phase, thorium metal and thorium dihydride. Equilibria in the thorium-hydrogen system up to the composition of thorium dihydride seem to be reversible and the system appears to behave in accord with the laws of classical thermodynamics. Except at extremely low pressures, the flux of hydrogen from the gas phase to the solid phase in this system is controlled by activity gradients in the solid phase unless the solid surface has been contaminated.

The reaction between thorium and hydrogen is governed by different rate laws depending on whether the hydrogen pressure is above or below the dissociation pressure of thorium dihydride. If the reaction occurs at a hydrogen

pressure above the dissociation pressure of the dihydride, the metal acquires a dihydride layer through which the hydrogen must diffuse. When the hydrogen pressure is maintained below the dissociation pressure of the dihydride, absorption occurs by the solution of hydrogen in thorium and the rate will depend on diffusion through the metal.

This investigation has determined the absorption rates over a temperature range from 350-700°C at pressures slightly above the dissociation pressure of the dihydride and up to 400 mm of mercury. An equation showing the correlation between the absorption rate and the rate of diffusion of hydrogen through the dihydride was derived and using the experimental absorption data, an estimate was made of the activation energy for diffusion. Values of the diffusivity of hydrogen in thorium, along with data on the solubility of hydrogen in thorium, would allow one to estimate the reaction rate between thorium and hydrogen at any pressure below the dissociation pressure of the dihydride, provided one assumed that the rate was not controlled by some surface phenomena. The rate of diffusion of hydrogen in the metal was investigated from 300° to 900°C. The activation energy for diffusion and the diffusivity at infinite temperature were determined, thereby providing an equation for the temperature dependence of the diffusivity, $D = D_o e^{-\frac{\Delta H}{RT}}$.

In recent years there has been an increased interest in

metal-hydrogen systems. Among those metals of primary interest which form hydrides are titanium, zirconium, and thorium. The absorption of hydrogen by thorium metal and the formation of thorium hydrides has been studied by several investigators, beginning as early as 1891, and their work is summarized in Gmelin's Handbuch (1). Nottorf (2) has obtained pressure-composition isotherms at various temperatures for the thorium-hydrogen system. His work indicated quite appreciable solid solubility of hydrogen in thorium and the formation of thorium dihydride as the first intermediate phase. The heat of formation of thorium dihydride was determined to be -35.2 kcal/mole. Mallett and Campbell (3), in a very similar study, found a heat of formation of -34.3 kcal/mole.

In both of these studies of the pressure-composition isotherms of the thorium-hydrogen system, the equilibrium hydrogen pressure over a two phase alloy of thorium metal and thorium dihydride was found to increase with increasing amounts of the hydride phase. This is a three phase system and, according to the phase rule, the number of components must be three in order for one degree of freedom to exist at constant temperature. Peterson et al. (4) have found this third component to be oxygen in the form of thorium dioxide inclusions which are soluble in thorium dihydride.

Rexer (5) has investigated the effect of carbon on pressure-composition isotherms. There is a marked decrease

in equilibrium hydrogen pressure over the thorium-hydrogen solid solution when carbon is present and the apparent solubility of hydrogen in thorium increases with increasing carbon content. The formation of a thorium-carbon-hydrogen compound is indicated and this possibility is being investigated.

Peterson and Westlake (6) have determined the solubility of thorium dihydride in thorium by a saturation technique. The heat of solution of thorium dihydride in Ames thorium was 6.6 kcal/gram atom which was in excellent agreement with the value of 6.3 kcal calculated from the data given by Mallett and Campbell (3) for thorium of similar purity. The solubility increased from about one atom percent hydrogen at $300^{\circ}C$ to above 20 atom percent at $800^{\circ}C$. At intermediate temperatures, the presence of carbon increased the apparent hydrogen solubility.

The effect of hydrogen on the mechanical properties of metals has become of great interest in recent years. Many metals are severely embrittled at room temperature, even by extremely small amounts of hydrogen. Peterson (7) has determined that hydrogen contents below 100 ppm do not affect the room temperature ductility of thorium but can change the strength and hardness significantly. At concentrations greater than 100 ppm hydrogen, additions of hydrogen reduced

the ductility of thorium, as measured by impact values and by reduction in area in tensile specimens.

It has become fairly well established that the mechanical properties of solid solutions are influenced by the interaction of solute atoms and dislocations. Therefore, the determination of the diffusivity of solute atoms has taken on new importance. The transport of solute atoms, by a temperature gradient, described by Markowitz and Belle (8) and by Shewmon (9) could be of extreme importance to reactor metallurgists. A temperature gradient across a moderator containing a metal hydride phase could induce a redistribution of not only the hydride phase but of solute atoms as well. Thus, the moderating property and the mechanical properties would vary along a line parallel to the temperature gradient.

The most commonly used technique in the study of absorption rates is the measurement of the amount of hydrogen absorbed as a function of time at constant temperature and pressure. The amount of hydrogen which has been consumed at any time can be determined by volume difference in a gas buret or by weight gain on a microbalance. Straetz and Draley (10) used a gas buret in studying the absorption of hydrogen by thorium. The apparatus used by Belle et al. (11) contained a pressure regulator which also measured the hydrogen consumed by volume. This method was used in studying the zirconium-hydrogen system and later, the uranium-hydrogen

system (12). Gulbransen (13) constructed a microbalance with which the absorption of hydrogen by zirconium was measured by weight gain (14).

The absorption of hydrogen by metals through a reaction product phase, at constant temperature and pressure, follows either the linear or the parabolic rate law. When the reaction continues without growth in thickness of the hydride phase, the amount of hydrogen entering the solid phases is proportional to the time. However, if the reaction product phase remains bonded to the metal so that the hydrogen must diffuse through this layer, and if the growth of this phase is proportional to the rate of absorption, then the absorption rate is parabolic. Uranium absorbs hydrogen according to the linear rate law (12), while zirconium absorbs hydrogen according to the parabolic rate law (11).

The rate at which massive thorium absorbs hydrogen at a pressure of one atmosphere was measured at temperatures between 100 and 500°C by Straetz and Draley (10). An induction time of two hours was required before Ames thorium absorbed hydrogen at 400°C. The reaction rate was reported as linear with time and was stated as mg of thorium reacted per sq cm of surface per hour. The values given were 168 mg/cm^2-hr at 400°C and 23.6 mg/cm^2-hr at 180°C. The induction period found by Straetz and Draley was thought to be a surface phenomenon caused by impurities in the metal.

Wagener (15), in a study of thorium powder as a getter, has
measured the rate of sorption of hydrogen at pressures between
10^{-7} and 10^{-3} mm of mercury. He found a heat of solution of
13 kcal/mole.

When absorption of hydrogen in massive metal follows
the parabolic rate law there is a relation between the absorp-
tion rate and the rate of diffusion of hydrogen through the
hydride. Gulbransen (16) has derived the equation

$$(4) \qquad\qquad \bar{C} = KD^{1/2}t^{1/2}$$

where $\bar{C}$ is the average concentration of the sample, K is a
constant and t is the time. Using this equation he was able
to determine a value of the diffusivity of hydrogen in zir-
conium hydride from absorption rate data. K was dependent on
the concentration gradient in the hydride and on the thickness
of the sample.

The steady state method has been used for the determina-
tion of the diffusivity of hydrogen in many metals. In this
method, hydrogen is maintained at a constant pressure, P_1,
on one side of a metal foil and at a lower constant pressure,
P_2, on the other side until a constant flux, J, is achieved.
The diffusivity can be determined from the value of this flux
as can be seen from the following derivation.

Fick's first law states that the flux through the foil
is proportional to the concentration gradient,

$$J = -D \frac{\partial C}{\partial x} . \tag{1}$$

If we assume that at constant P_1, P_2, and temperature, the concentration gradient in the x direction is constant for all points inside the foil, then

$$\frac{\partial C}{\partial x} = \frac{C_1 - C_2}{\Delta x} \tag{2}$$

where C_1 and C_2 are the surface concentrations corresponding to P_1 and P_2, respectively, and Δx is the thickness of the foil. If we now assume that C_1 and C_2 are equilibrium concentrations within the solubility range, Sievert's law applies.

$$C_1 = S \sqrt{P_1} \quad \text{and} \quad C_2 = S \sqrt{P_2} ,$$

where S is a solubility constant. Thus

$$J = -SD \frac{\sqrt{P_1} - \sqrt{P_2}}{\Delta x} . \tag{3}$$

The solubility constant can be obtained from pressure-composition isotherms, the other quantities can be measured during the experiment, and a value of D calculated. Various experimental devices which can be used are described by McGill and Sibbitt (17). Very erratic results can be obtained by this method when the metal of interest is subject to surface contamination. Davis (18, 19) has found that many of the diffusivity values obtained for both palladium and uranium were in error because the flux was controlled by some surface reaction. Since thorium reacts with so many of the elements which exist as gases at room temperature, to

form insoluble compounds at the surface, the steady state method did not seem likely to produce reliable results in the study of the diffusion of hydrogen in thorium.

The non-steady state evolution method for determining the diffusivity of hydrogen in metals depends on the measurement of the evolution rate of hydrogen from a specimen of massive metal of simple geometry and known initial hydrogen concentration. The non-steady state absorption technique involves determination of the concentration gradient in a specimen of simple geometry and known initial hydrogen concentration after absorption has occurred for a known time. Solutions of Fick's differential equation can be adapted for different specimen geometries and various experimental approaches. Both the evolution method and the absorption method were used in this investigation.

Eichenauer and Pebler (20) were able to calculate the diffusivity of hydrogen in aluminum and copper from observation of the evolution rates of hydrogen from the metals into closed volumes which were initially evacuated. Another evolution technique, employed by Hill and Johnson (21), involves measuring the flow rate of hydrogen evolved from nickel through a constriction into a dynamic vacuo.

A more conventional technique has resulted from considerations of heat flow by Carslaw and Jaeger (22). The solution of the differential equation which expresses Fick's

second law of diffusion was demonstrated for radial heat flow

into an infinitely long cylinder with the surface temperature

and D constant. Theoretical curves of $\frac{T - T_O}{T_s - T_O}$ vs r/a were

plotted for various values of Dt/a^2,

where T = temperature at radius r at time t,

T_O = uniform temperature of the cylinder at t = 0,

T_s = temperature at the surface of the cylinder at t > 0,

and a = radius of the cylinder.

Crank (23) has pointed out the application of these

theoretical curves to mass diffusion problems. After a

constant concentration has been maintained at the surface of

a cylinder for a time t, the specimen can be quenched and

concentric sections can be analyzed to provide $\frac{C - C_O}{C_s - C_O}$

vs r/a data, where C_s may be unknown. By trial and error a

value of C_s is found such that the data may be fit to one of

the theoretical curves, thereby giving a value of Dt/a^2.

Since t and a are measured experimentally, D is determined.

This method had been used with notable success in studying

the diffusion of nitrogen in beta zirconium (24), hydrogen

in alpha zirconium (25), and hydrogen in alpha and beta

titanium (26), and provided very satisfactory results in this

study.

Barrer (27) has gathered solutions of Fick's differential

equation for many of the possible boundary conditions and

geometric configurations. A cylindrical specimen has been used in many diffusion investigations because of the ease in forming this shape. Starting with

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) , \qquad (4)$$

for unidirectional flow, if we assume D is constant at constant temperature, then D may be brought outside the differential,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} . \qquad (5)$$

Considering three dimensional flow and transforming to cylindrical coordinates (r, Θ, z), we have

$$\frac{\partial C}{\partial t} = D \nabla^2 C = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} \right) . \qquad (6)$$

The equation does not contain Θ because the rate of flow is independent of Θ.

The solution to equation (6) has undergone a simplifying approximation by Geller and Sun (28) which allows one to estimate the diffusivity from a plot of $\frac{\partial \overline{C}}{\partial t}$ vs t when evolving hydrogen from metal cylinders into a dynamic vacuo. $\frac{\partial \overline{C}}{\partial t}$ is the time rate of change of the average composition of the sample. Hill and Johnson (29) have used the method successfully in studying the diffusion of hydrogen in iron.

Because the average concentration of the sample is more readily measured experimentally than $\frac{\partial \overline{C}}{\partial t}$, the following

solution of equation (6) and the simplification due to Demerez et al. (30) were used in this study. Evolution of hydrogen from a finite cylinder, where $C = C_0$ at $t = 0$, and $C_s = 0$ at $t > 0$, is characterized by equation (7), which is a particular solution of equation (6).

$$\frac{\bar{C}}{C_0} = \frac{32}{\pi^2}\left[\sum_{n=0}^{\infty} e^{\frac{-(2n+1)^2 \pi^2 \frac{Dt}{s^2}}{(2n+1)^2}}\right]\left[\sum_{n=1}^{\infty} e^{\frac{-\beta_n^2 \frac{Dt}{a^2}}{\beta_n^2}}\right] \qquad (7)$$

where C_s = surface concentration,

$\bar{C}$ = average composition at time t,

C_0 = initial uniform composition,

t = time in seconds,

D = diffusivity in cm^2/sec,

s = cylinder length in cm,

a = cylinder radius in cm

and β_n is a root of $J_0(\beta) = 0$, where J_0 is the zeroth order Bessel function. $\bar{C}/C_0$, t, s, and a are all obtainable, experimentally.

Examination reveals that the terms of both infinite series in equation (7) are strictly monotone decreasing, that is, each term is smaller than the preceding one. If t is large enough, for given values of s and a, all terms after the first in each series will become negligible and one can write

$$\frac{\overline{C}}{C_o} = \frac{32}{\pi^2}\left[e^{-\pi^2 \frac{Dt}{s^2}} \right]\left[\frac{e^{-\beta_1^2 \frac{Dt}{a^2}}}{\beta_1^2} \right].$$ (8)

Since $\beta_1 = 2.405$ (31), equation (8) becomes

$$\log \frac{\overline{C}}{C_o} = \log (0.56) - D\left(\frac{4.28}{s^2} + \frac{2.52}{a^2} \right) t .$$ (9)

Therefore, for sufficiently large values of t, a plot of log $\overline{C}/C_o$ vs t should result in a straight line, the slope of which is $- D\left(\frac{4.28}{s^2} + \frac{2.52}{a^2} \right)$. This method has provided very satisfactory results for Demerez et al. (30) in investigating the diffusion of hydrogen in mild steel, and for Griffith and Mallett (32), and Albrecht and Mallett (33) in studies of the evolution of hydrogen from titanium.

II. EXPERIMENTAL

A. Materials

Thorium of two purity levels was used in this investigation. As-cast Ames thorium was reduced 50 percent by rolling to a thickness of 11.5 mm and swaged into a 10 mm diameter rod having its axis in the direction of rolling. Crystal bar thorium, made in the Ames Laboratory, was arc-melted under helium into a bar. This bar was swaged to a rod having a diameter of 9 mm. After being vacuum annealed, the Ames thorium and the crystal bar thorium had diamond pyramid hardness numbers of 69 and 35, respectively. Results of the analyses of these two types of thorium are shown in Table 1. Carbon was determined by combustion and nitrogen by the Kjeldahl method. The oxygen in Ames thorium was determined by weighing the hydrochloric acid insoluble residue as thorium dioxide, whereas the oxygen in the crystal bar thorium was determined by vacuum fusion. All other elements were determined spectrographically.

Cylindrical specimens were machined to the desired dimensions after the lathe and the cutting tool had been carefully cleaned to avoid contamination of the sample surface by oil. Abraded specimens produced inconsistent results in the evolution experiments apparently due to surface contamination. Samples used for the study of the absorption

Table 1. Analysis of thorium metal

Element	Crystal bar Th	Ames Th
	(ppm)	(ppm)
C	145	410
N	70	70
O	60	1300
Fe	< 20	130
Mn	--	20
Cr	20	20
Ni	20	20
Al	50	40
Ca	< 25	50
Mg	--	20
Si	--	55
Be	--	170

rate were approximately 3.5 mm long and measured about 6.5 mm in diameter. Dimensions of the specimens used in determining diffusivity by the evolution technique varied somewhat, but the average diameter and length were 8 mm and 20 mm, respectively. For the study of diffusion by the absorption technique, cylinders were used which had diameters of about 9 mm and lengths of about 60 mm.

B. Apparatus

A modified Sieverts apparatus was used for the entire study. The principle parts of the apparatus were a hydrogen source, a fused silica tube which contained the sample during an experiment, a device for regulating the hydrogen pressure in the fused silica tube, a manometer for measuring this pressure, and a mercury diffusion pump which pumped gas from the fused silica tube into a calibrated volume. A schematic diagram of the apparatus is shown in Figure 1.

The Vycor tube, A, contained uranium trihydride which served as the source of pure hydrogen. Heating to about $400^{o}C$ with a flame caused dissociation of the hydride, whereas compounds of uranium with impurities in the tank hydrogen remained stable.

The device at B was a modification of a gas buret and pressure regulator described by Belle et al. (11). It was completely immersed in a constant temperature water bath. Hydrogen, from the hydrogen generator, was stored over mercury in tube P. Tube Q was open at the top to the atmosphere. The three-way, high vacuum stopcock on the mercury pot T was connected to a Duo-Seal type 1400 mechanical vacuum pump and to a nitrogen tank so that the mercury columns in tubes P and Q could be kept level by manipulation of this stopcock. Hydrogen, at atmospheric pressure, was thus
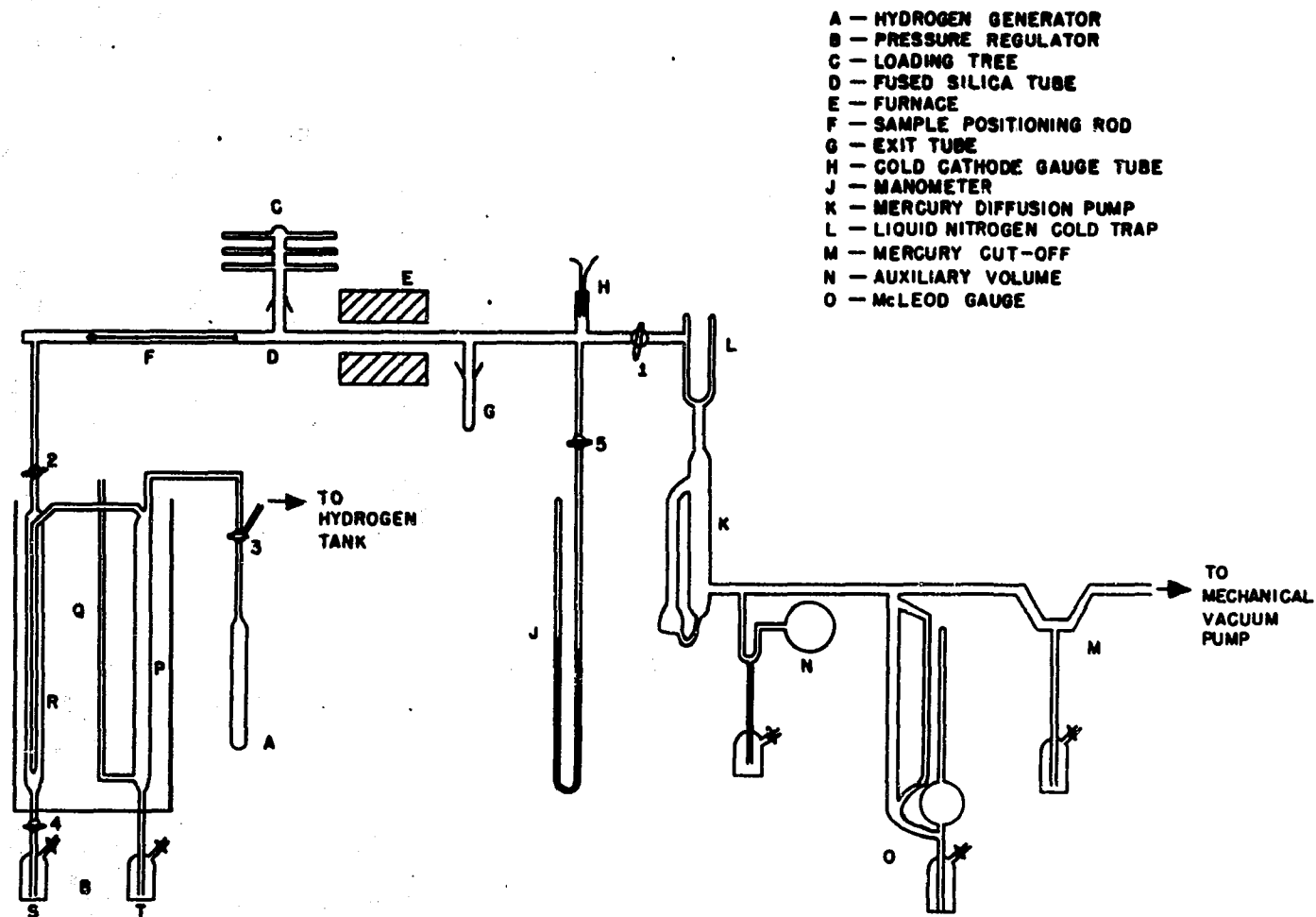
A — HYDROGEN GENERATOR
B — PRESSURE REGULATOR
C — LOADING TREE
D — FUSED SILICA TUBE
E — FURNACE
F — SAMPLE POSITIONING ROD
G — EXIT TUBE
H — COLD CATHODE GAUGE TUBE
J — MANOMETER
K — MERCURY DIFFUSION PUMP
L — LIQUID NITROGEN COLD TRAP
M — MERCURY CUT-OFF
N — AUXILIARY VOLUME
O — McLEOD GAUGE

TO HYDROGEN TANK

TO MECHANICAL VACUUM PUMP

Figure 1.   Schematic diagram of modified hydrogen Sieverts apparatus

17

supplied to the capillary tube inside tube R. The capillary tube was immersed in mercury and hydrogen was bubbled into tube R through this constant head, thus maintaining a constant pressure in tube R. The magnitude of the head could be adjusted by manipulation of the three-way stopcock on mercury pot S. Tubes P and R were 85 cm long and had inside diameters of 25 mm. Tube Q had an inside diameter of 10 mm. A scale, graduated in millimeters, was visible behind all three tubes.

Specimens were placed in the loading tree, C, each branch of which contained a cylinder of iron so the thorium specimen could be manipulated from the outside by a magnet. The loading tree was connected to the fused silica tube, D, by a standard taper sealed with Apiezon W wax. A specimen which was pushed from the tree into the fused silica tube was then positioned at the center of the furnace by a fused silica push-rod, F, which contained a cylinder of iron in one end. Samples were removed from the system by pushing them into the exit tube, G, which was connected to the fused silica tube by a standard taper sealed with Apiezon W wax.

The Multiple Unit, type 70-T, resistance furance, E, was 12 inches long. An alundum tube, four inches long and having an inside diameter of 7/8 inch and an outside diameter of 1 1/4 inches, was placed at each end of the cylindrical furnace cavity. At the center was a type 309 stainless steel

tube, 4 inches long, having an inside diameter of 1 1/16 inches and an outside diameter of 1 1/4 inches. This arrangement provided a uniform temperature, within two centigrade degrees, over a distance of 1 1/2 inches on each side of the furance center. The temperature of the furnace was maintained constant by the use of a Raytheon 500 watt voltage stabilizer. The temperature was adjusted by varying the voltage output of a type 116U-2D Powerstat variable transformer. A chromel-alumel thermocouple was positioned to contact the outside of the fused silica tube at the center of the furnace.

During evacuation of the fused silica tube, the pressure was measured by a cold cathode tube, H, connected to a Miller Laboratories cold cathode vacuum gauge, model 100-A. Higher pressures, such as those used in absorption runs, were measured by the use of the manometer, J. A Duo-Seal type 1405 mechanical fore-pump and a Consolidated Vacuum Corporation model GHG 15-01, three stage mercury diffusion pump, K, were used to evacuate the fused silica tube. A dynamic vacuum of $5x10^{-7}$ mm of mercury could be achieved when the cold trap, L, was filled with liquid nitrogen. Although they are not shown on the diagram, liquid nitrogen cold traps prevented mercury vapor from the pressure regulator and the manometer from entering the fused silica tube.

The total volume of the fused silica tube, loading tree, exit tube and manometer was approximately 700 ml.

The mercury cut-off at M made it possible to collect hydrogen, pumped from the fused silica tube by the mercury diffusion pump, in the calibrated volume between the cut-off and the mercury diffusion pump. The pressure of the collected gas was measured by the McLeod gauge, O. This gauge was designed to measure pressures between one micron and 4.5 mm of mercury. The collection volume was 670 ml. This could be increased to 1756 ml by opening the mercury cut-off to the auxiliary volume, N. All the mercury pots in the system were connected to the same Duo-Seal type 1400 mechanical pump for manipulation of mercury levels.

C. Operating Procedure

1. Measurement of absorption rates

After being machined, a specimen was washed three times in trichlorethylene and rinsed three times in acetone. It was then placed in the loading tree and the tree was sealed in position. With stopcocks 2 and 5 open, and stopcock 3 open toward the pressure regulator, the system was evacuated through stopcock 1, a 15 mm stopcock. The mercury in tube R was kept just below the capillary tip. Careful adjustment of the mercury levels of tubes P and Q was necessary during

evacuation to avoid forcing mercury out the top of tube P.

During evacuation, the furnace was kept at 800°C and the outgassing of the system was hastened by flaming. When a pressure of 5×10^{-7} mm of mercury was reached, the furnace was cooled to the temperature of interest. The mercury in tube R was adjusted to provide hydrogen at the desired pressure and stopcock 4 was closed. No surface contamination effects were observed during an absorption experiment if the static pressure was less than 1×10^{-5} mm of mercury after closing stopcock 1. The cold cathode gauge was shut off and hydrogen was generated by heating the uranium trihydride in tube A. The mercury levels in tubes P and Q were adjusted so that tube P was nearly full of hydrogen when the mercury columns in tubes P and Q became level. At this time, heating was discontinued and stopcock 3 was closed.

During the filling of tube P, hydrogen bubbled through the mercury in tube R so that the hydrogen in the fused silica tube was at the desired pressure when stopcock 3 was closed. The height of the mercury column in tube P was recorded. The sample was dropped into the furnace tube and pushed to the center of the furnace. As hydrogen was absorbed by the thorium sample, hydrogen from tube P bubbled through tube R to maintain a constant pressure in the fused silica tube. The flow of nitrogen into the mercury pot T was regulated to keep the mercury columns in tubes P and Q level.

The height of the mercury column in tube P was recorded at
intervals of one or two minutes. The cross sectional area of
tube P had been calibrated so the volume of hydrogen absorbed
could be calculated from the change in height. The number
of moles of hydrogen was calculated by the use of the perfect
gas law. The data recorded were translated into time vs mg
of hydrogen absorbed per sq cm of sample surface.

2. **Determination of diffusion rates by
   the non-steady state evolution technique**

Cylindrical specimens of thorium were charged with
hydrogen to concentrations below the solubility limit and
allowed to equilibrate. The pressure over the sample was
then reduced to essentially zero. The progress of the evolu-
tion of hydrogen was followed by collecting the evolved gas
in a closed volume and recording the pressure after known
time intervals. These data were analyzed graphically to ob-
tain the diffusivity of hydrogen in thorium.

The specimens were washed and inserted in the loading
tree as in the measurement of absorption rates. The system
was also evacuated in the same manner. When the system had
reached a pressure of 5×10^{-7} mm of mercury, stopcock 2 was
closed. The desired furnace temperature was obtained and
stopcock 1 was closed. After the cold cathode gauge had
been shut off, hydrogen was generated and stored in the pres-

sure regulator. Stopcock 3 was closed and stopcock 2 was opened to introduce the desired pressure in the fused silica tube. The desired pressure was determined from the intended initial hydrogen concentration of the specimen, the weight of the sample and the volume of the system.

The specimen was pushed to the center of the furnace and allowed to equilibrate with hydrogen in the gas phase. Two hours were allowed at $900^{\circ}C$ and eight hours at $600^{\circ}C$. Subsequent consideration of the diffusivity of hydrogen in thorium verified these as adequate times for the attainment of uniform concentration throughout the sample.

When the furnace section was evacuated to initiate evolution, the gas in equilibrium with the metal was pumped to the collection volume and therefore increased all subsequent pressure readings by the same amount. In order to correct for this, stopcock 5 was closed before evacuating, thus isolating the manometer while filled with hydrogen at the equilibrium pressure. This hydrogen was later pumped into the collection volume and measured in order to determine the hydrogen pressure in the furnace section. The mercury cut-off at M was closed to retain the gas pumped by the mercury diffusion pump into the collection volume. Stopcock 1 was opened, evolution began, and time was measured on a stopwatch calibrated in tenths of a second. The hydrogen pressure in the collecting volume was measured by the McLeod

gauge at time intervals of two or three minutes. When evolution became very slow, the temperature of the furnace was raised to approximately 840°C and held until no further evolution was detected.

After the collection volume had been evacuated through the mercury cut-off, M, and the specimen had been pushed into the exit tube, the cut-off was again closed and stopcock 5 was opened. The hydrogen from the manometer was collected and the pressure was measured. Since the volumes of the manometer and of that part of the system between stopcocks 1 and 2 were known, it was possible to calculate the amount of hydrogen in the gas phase in equilibrium with the specimen at t = 0. The ratio of the average concentration of hydrogen in the sample, $\overline{C}$, at time t to the initial concentration, C_o, was equal to

$$\frac{(P-p_c) - (p-p_c)}{P - p_c} , \quad or \quad \frac{P - p}{P - p_c} ,$$

where P was the pressure in the collection volume when evolution was complete, p was the pressure at time t, and p_c was the pressure correction due to the hydrogen in the gas phase at equilibrium.

3. Determination of diffusion rates by
    the non-steady state absorption technique

Thorium cylinders, of known dimensions, were allowed to absorb hydrogen. The reaction produced a thin dihydride

surface layer. Hydrogen diffused from this layer and established a concentration gradient in the metal. The specimen was quenched and concentric sections were analyzed. These data, indicative of the concentration gradient, were treated graphically to determine the diffusivity of hydrogen in thorium.

Freshly machined thorium cylinders were cleaned in the same way as those used in determining absorption rates. After the sample was inserted in the loading tree, the furnace tube was evacuated, with stopcocks 2 and 5 open, to a pressure of 5×10^{-7} mm of mercury. Stopcock 2 was closed, and the specimen was pushed to the center of the furnace and annealed at $800^\circ C$ for two hours in a dynamic vacuum.

An estimate was made of the amount of hydrogen necessary to cover the specimen with a uniform hydride layer, the thickness of which would be about two percent of the radius of the cylinder. This amount of hydrogen was generated and stored in the pressure regulator. When the sample had been cooled to the temperature of interest, the cold cathode gauge was shut off and hydrogen was allowed to enter the furnace tube. Stopcock 2 was manipulated to maintain the pressure over the thorium about 2 mm of mercury above the dissociation pressure of the hydride at that temperature until the desired amount of hydrogen had reacted with the sample.

The time necessary to produce a satisfactory concentra-

tion gradient between the thorium-thorium hydride interface and the axis of the cylinder was estimated from theoretical plots (22) of C/C_g vs r/a for various values of Dt/a^2. The value of D, used to obtain this estimate, was obtained from the log D vs $1/T$ plot of the evolution method data. This time varied from 15 minutes at $600^{\circ}C$ to nine hours at $300^{\circ}C$.

When diffusion had occurred for the desired time, the sample was quickly pushed from the furnace and air cooled. Ten millimeter lengths were cut from each end of the cylinder. The distribution of hydrogen in the remaining cylinder could be considered the result of radial diffusion only. The cross section of each end was inspected microscopically for uniform thickness of the hydride layer. The hydride layer was machined from the cylinder and discarded. Eight tubular sections, concentric with the cylinder, were machined from the cylinder and the inside and outside diameters of each section were recorded.

The turnings from each section were pressed into compacts using a pressure of 100,000 psi at room temperature. Each section was then analyzed for hydrogen by warm vacuum extraction. After the furnace tube was evacuated with stop-cocks 2 and 5 closed, the compacts from a section were pushed into the furnace. The hydrogen in the sample was evolved rapidly at $840^{\circ}C$ and the total amount of hydrogen emitted by each section was measured in the collection volume.

III. RESULTS AND DISCUSSION OF RESULTS

A. Absorption Rate of Hydrogen in Thorium

Absorption of hydrogen by crystal bar thorium was found to follow the parabolic rate law when the hydrogen pressure was greater than the dissociation pressure of thorium dihydride. Microscopic examination following absorption showed a hydride layer of uniform thickness on each specimen. Plots of the weight of hydrogen absorbed per sq cm of sample surface vs the square root of the time were straight lines. Figure 2 shows three typical plots. The failure of each line to pass through the origin is due to the slower absorption before the sample reached the furnace temperature. The slope of each plot was called the absorption rate, k. Table 2 gives the results obtained for various temperatures and pressures. Absorption which follows the parabolic rate law must be controlled by diffusion through a growing reaction product layer.

Pressure-composition isotherms for the thorium-hydrogen system (2) indicate that thorium dihydride exists over a range of composition. Therefore, during absorption, the hydrogen concentration in the hydride at the hydride-gas interface would be greater than the hydrogen concentration
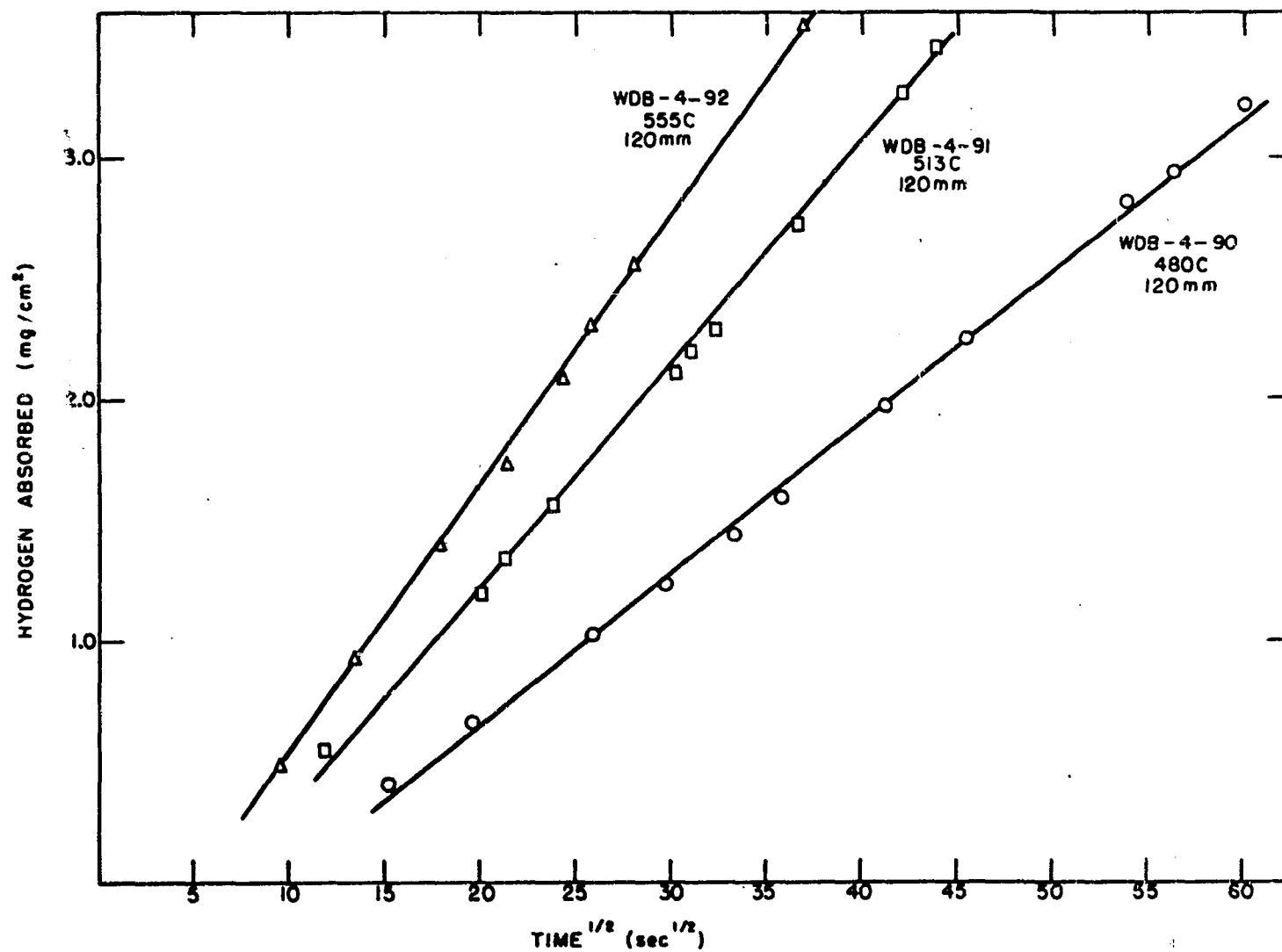
Figure 2. Absorption of hydrogen by thorium

Table 2. Absorption rates of hydrogen in annealed crystal
bar thorium

Temperature (^oC)	Pressure (mm of Hg)	Absorption rate (mg/cm^2-sec$^{1/2}$)
347	12	.018
350	117	.017
375	14	.020
375	116	.022
404	118	.029
410	113	.039
450	48	.045
449	49	.046
450	115	.053
450	115	.053
450	115	.053
450	119	.056
450	119	.056
450	119	.057
452	246	.052
449	246	.051
452	249	.053
452	400	.055
476	113	.066
480	118	.062
513	119	.092
548	7	.070
550	14	.074
551	15	.070
555	40	.098
555	116	.112
556	400	.124
552	401	.123
600	36	.101
600	399	.160
700	52	.049
700	99	.112
700	399	.190

in the hydride at the metal-hydride interface. This produces
the concentration gradient necessary for diffusion of hydro-
gen through the hydride layer. An increase in the hydrogen
pressure, at constant temperature, would increase the equi-
librium hydrogen concentration at the surface, but would
not affect the equilibrium concentration at the metal-hydride
interface. Therefore one might expect the absorption rate
to increase with pressure.

Figure 3 shows k as a function of $(P - P_d)$ for some of
the temperatures studied. P is the hydrogen pressure during
the reaction, while P_d is the dissociation pressure of the
dihydride in equilibrium with thorium metal. The values of
P_d, estimated from Nottorf's pressure-composition isotherms
shown in Figure 4, were 45 mm of mercury at $700^{\circ}C$, 6 mm at
$600^{\circ}C$, 2 mm at $550^{\circ}C$, and negligible at lower temperatures.
When the pressure dependence of k is plotted in this manner,
k should approach zero as P approaches P_d. This behavior is
strongly indicated by the curves in Figure 3. At 350 and
$450^{\circ}C$, the absorption rate was independent of pressure over
the pressure range which was studied. At higher tempera-
tures, the absorption rate increased with pressure very
rapidly at low pressures and thereafter increased rather
slowly with further increase in pressure.

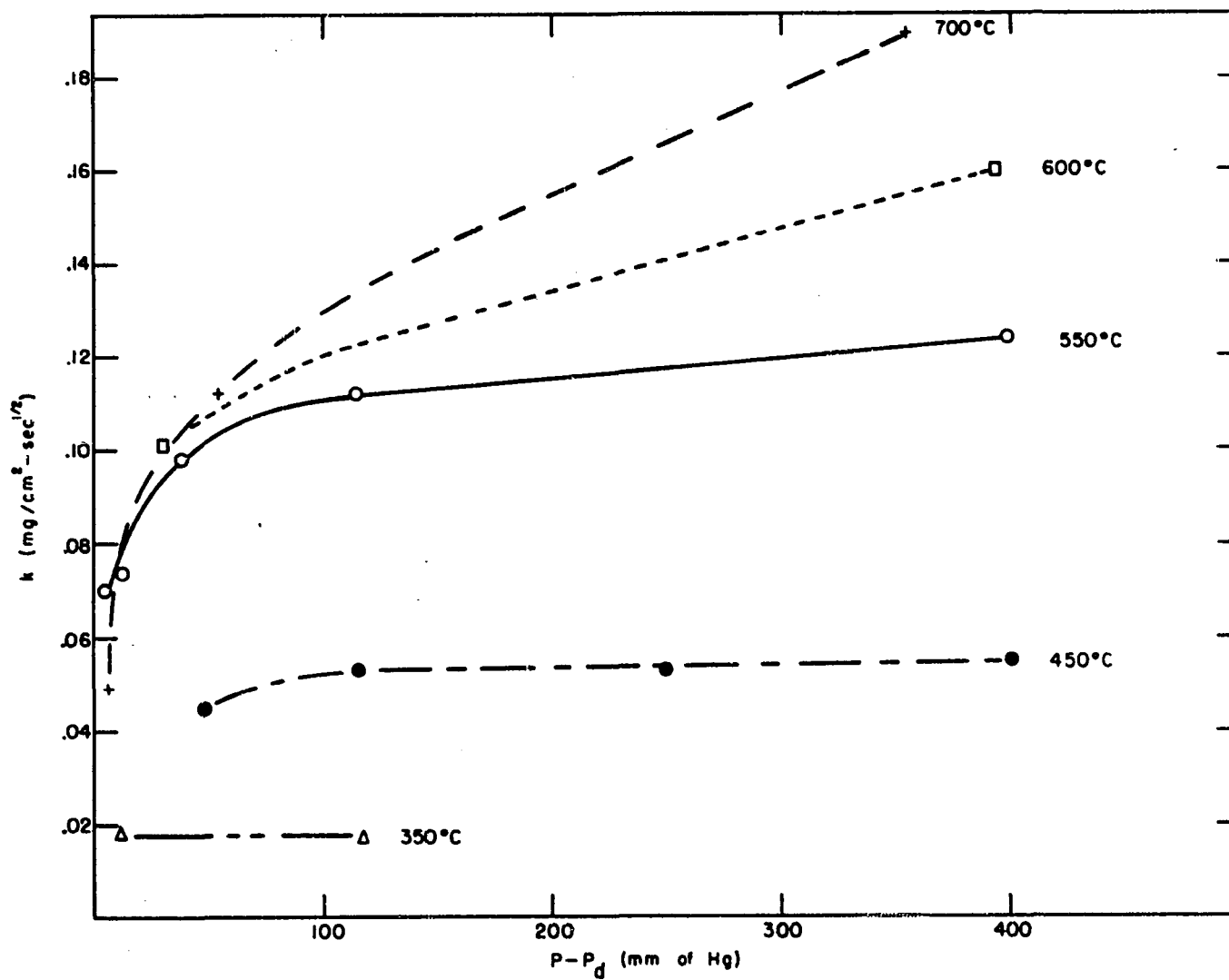The relationship between the absorption rate and the

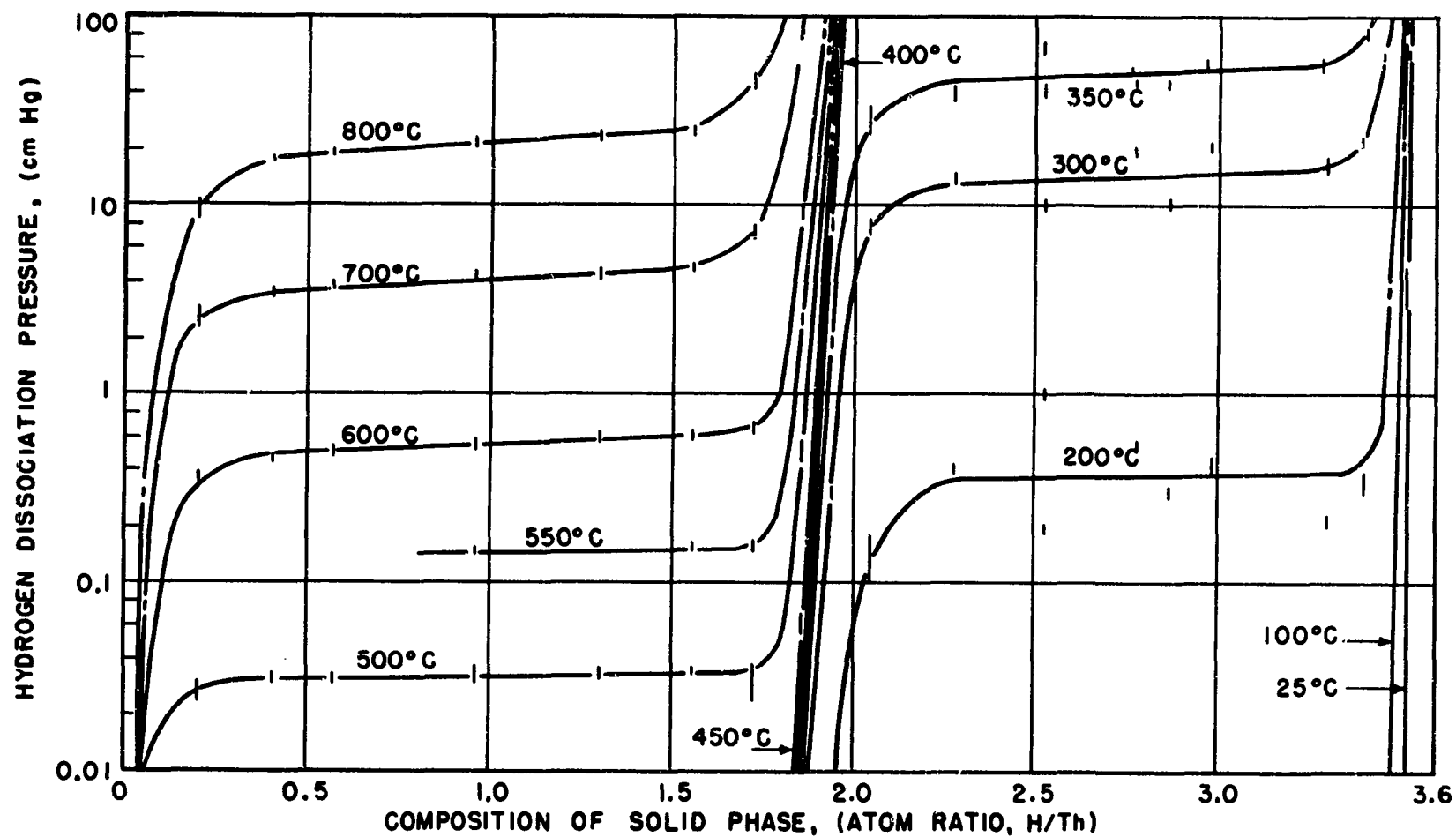Figure 3. Variation of the absorption rate with pressure

Figure 4. Pressure-composition isotherms of the thorium-hydrogen system (2)

diffusion rate of hydrogen in the hydride can be derived from the parabolic rate law,

$$m = kt^{1/2} . \tag{10}$$

If J equals the flux of hydrogen through one sq cm of surface, then

$$J = \frac{dm}{dt} = 1/2 \, kt^{-1/2} \tag{11}$$

Fick's first law states

$$J = D \, \frac{\partial C}{\partial x}. \tag{12}$$

If the surface concentration and the concentration of the hydride at the metal-hydride interface are assumed to be constant for a given temperature and pressure, and if we assume that for any given time the concentration gradient in the x direction is a constant for all points in the hydride layer, then $\frac{\partial C}{\partial x} = \frac{\Delta C}{x}$, where ΔC is the difference in hydrogen concentration across the hydride, and x is the thickness of the layer. Therefore, from equations (11) and (12),

$$1/2 \, kt^{-1/2} = D \, \frac{\Delta C}{x} . \tag{13}$$

Consideration of the solubility of hydrogen in thorium (6), the diffusivity of hydrogen in thorium, and the short duration of the absorption runs showed that the amount of hydrogen which entered the thorium metal was very small. Hence, little error was made in assuming x was proportional to m, or x = Km.

Tne density of thorium dihydride, calculated from the lattice constants (5), is 9.45×10^3 mg/cm^3. Therefore,

$$m = \left(\frac{\text{mol wt of hydrogen}}{\text{mol wt of ThH}_2}\right)\left(9.45 \times 10^3 \text{ mg/cm}^3\right)(x \text{ cm}) \, ,$$

$$m = \frac{2}{234} \cdot 9.45 \times 10^3 \, x = 80.6 \, x \, ,$$

and $x = 0.0124$ m.

Because $m = kt^{1/2}$,

$$x = 0.0124 kt^{1/2} \, . \tag{14}$$

This expression for x may be substituted into equation (13) to give

$$1/2 \, kt^{-1/2} = \frac{D \Delta C}{0.0124 kt^{1/2}} \, .$$

Therefore,

$$k^2 = \frac{D \Delta C}{0.0062} \tag{15}$$

If the temperature dependence of D can be expressed by

$$D = D_o e^{\frac{-\Delta H}{RT}} \, , \text{ then}$$

$$k^2 = \frac{\Delta C}{.0062} D_o e^{\frac{-\Delta H}{RT}} \, , \tag{16}$$

where D_o is the diffusivity of hydrogen in the hydride at infinite temperature and ΔH is the energy of activation for diffusion.

Figure 5 is a plot of log k^2 vs $10^3/T$ at a pressure of about 120 mm of mercury. The linearity of the plot indicates that at temperatures below 550°C, $D_o \Delta C$ is virtually
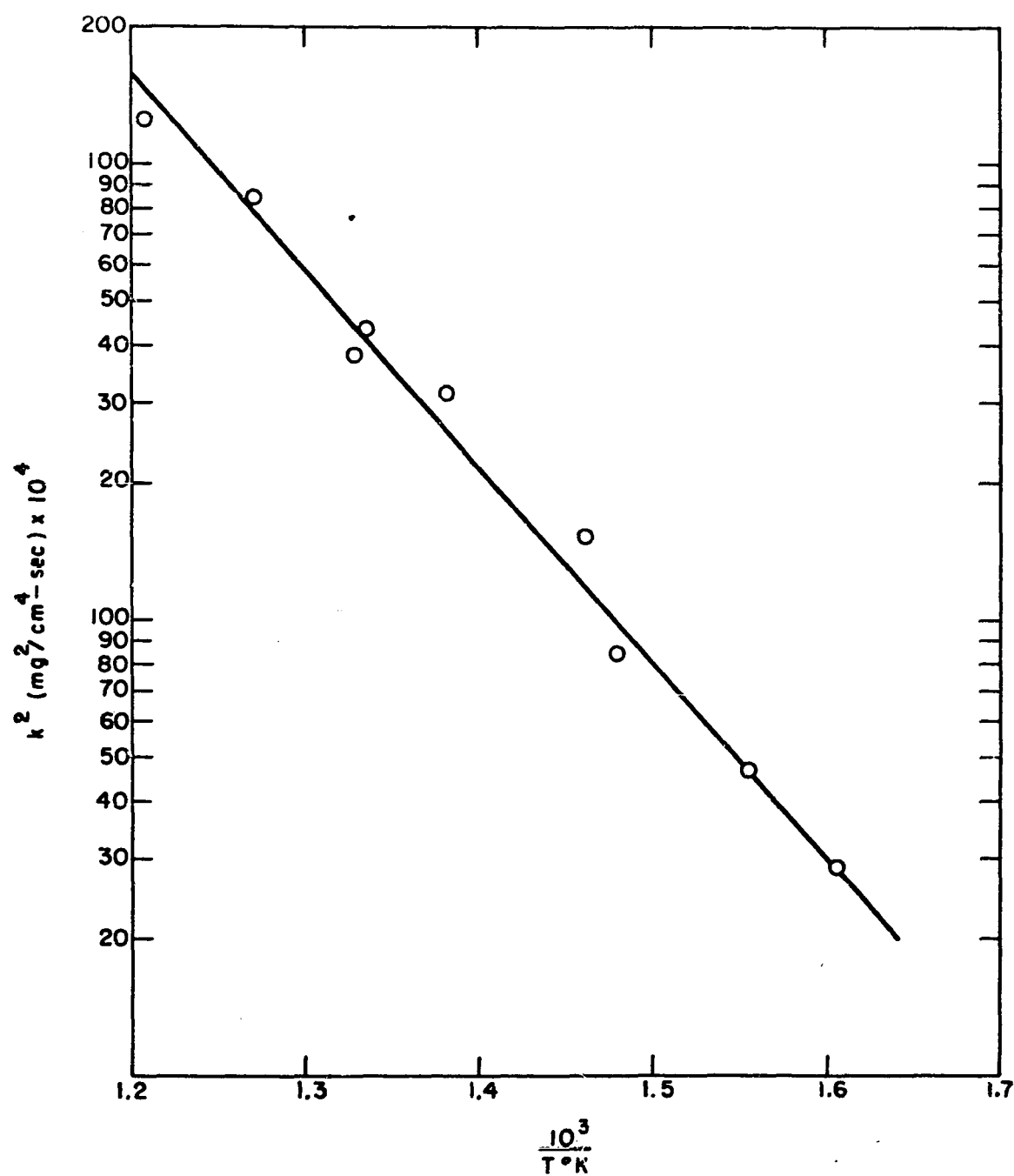
Figure 5. Variation of absorption rates with temperature at a pressure of 120 mm of mercury

constant at this pressure. Figure 3 leads one to predict
that the same would be true at all pressures greater than
120 mm of mercury. From the slope of the straight line,
ΔH was found to be approximately 19.6 kcal. Determination
of D_0 was impossible because ΔC was not known. Accurate
values of ΔC would be very difficult to obtain from
pressure-composition isotherms over the composition range of
the hydride because of the extreme dependence of the equilib-
rium hydrogen pressure on the composition of the hydride.

Nottorf's isotherms (2) show an increased range of
hydrogen content in the dihydride with increasing temperature
for a given maximum hydrogen pressure. Thus, from equation
(16), one could predict an increased pressure dependence of
k with increasing temperature. This prediction is verified
by the curves in Figure 3.

An appreciable induction time was noted in an earlier
study (10) of the absorption rate of hydrogen by thorium.
This was undoubtedly the time necessary for the diffusion of
hydrogen through a contaminant film, and the subsequent rup-
ture of this film by the formation of thorium hydride. With
careful handling of the specimens, no induction times were
noted in this study when a static pressure of 10^{-5} mm of mer-
cury was achieved before hydrogen was allowed to enter the
furnace tube. Straetz and Draley (10) measured absorption
rates between 100 and 500°C at a hydrogen pressure of one

atmosphere. They reported a linear rate of absorption. The reaction product flaked off the metal so this linear rate would be expected. At temperatures below 400°C, the higher hydride of thorium is stable at one atmosphere hydrogen pressure (2) and was probably the reaction product in many of the experiments run by Streetz and Draley.

In this investigation temperatures and pressures were such that the only reaction product was thorium dihydride. The dihydride layer remained bonded to the crystal bar thorium at all temperatures studied and to the Ames thorium at temperatures of 550°C and above. A layer of dihydride, 45 microns thick, remained bonded to Ames thorium even at 300°C, but thicker layers cracked at 450°C and below. The large oxide inclusions in Ames thorium may be stress points at which fracture occurs in the thicker layers. When cracking occurred, absorption followed neither the parabolic nor the linear rate law.

Table 3 contains the absorption rate data obtained for Ames thorium and for crystal bar thorium in the swaged condition. Comparison of Tables 2 and 3 indicates that neither the impurities in Ames thorium nor the microstructure has very much effect on the absorption rate at the temperatures and pressures investigated.

The temperature range of this investigation was limited by the absorption rates. Above 700°C, absorption occurred so

Table 3. Absorption rates of hydrogen in Ames thorium and in swaged crystal bar thorium

Material	Temperature ($^\circ C$)	Pressure (mm of Hg)	Absorption rate ($mg/cm^2-sec^{1/2}$)	Absorption rate for annealed crystal bar thorium ($mg/cm^2-sec^{1/2}$)
Ames Th	550	120	.121	.119[a]
"	553	120	.123	.119[a]
"	602	403	.169	.160[b]
"	699	399	.186	.190[b]
Swaged crystal bar Th	400	123	.029	.030[a]
"	452	120	.049	.051[a]
"	502	121	.075	.080[a]

[a]Estimated from Figure 5.

[b]Table 2.

rapidly that accurate measurements of the hydrogen consumed could not be made. At temperatures lower than $350^\circ C$, the time necessary for a run became prohibitive.

B. Diffusivity of Hydrogen in Thorium

1. Non-steady state evolution

When one plots the log $\bar{C}/C_0$ vs t data, calculated after experimental measurement of the evolution of hydrogen from

thorium cylinders, a curve characteristic of equation (7) is obtained. As t becomes sufficiently large, the points fall on the curve of equation (9). Thus, the straight line portion of each evolution curve has a slope equal to $-D(\frac{4.28}{s^2} + \frac{2.52}{s^2})$, and extrapolates to $\bar{C}/C_0 = 0.56$ at $t = 0$. Figure 6 shows four typical curves obtained experimentally. All the diffusivities given in Table 4 were determined by this method.

The observed diffusion coefficients were found to vary with the initial hydrogen content of the specimen. Since equation (7) is a particular solution of equation (5), and equation (5) is based on the assumption that D is constant with varying concentration at constant T, one would not expect the experimental curves to satisfy equation (9) if the diffusivity proved to be concentration dependent. However, in this study, straight line portions of the evolution curve were observed for large values of t, even though the value of D for a given temperature varied with the initial composition, C_0. According to Albrecht and Mallett (33), this behavior is to be expected when the concentration dependence of the diffusivity is not extreme. The value of D obtained by the evolution method can be considered the average D over the concentration range of the experiment.

In Figure 7, the diffusivities given in Table 4 are plotted against the initial hydrogen content for each of the
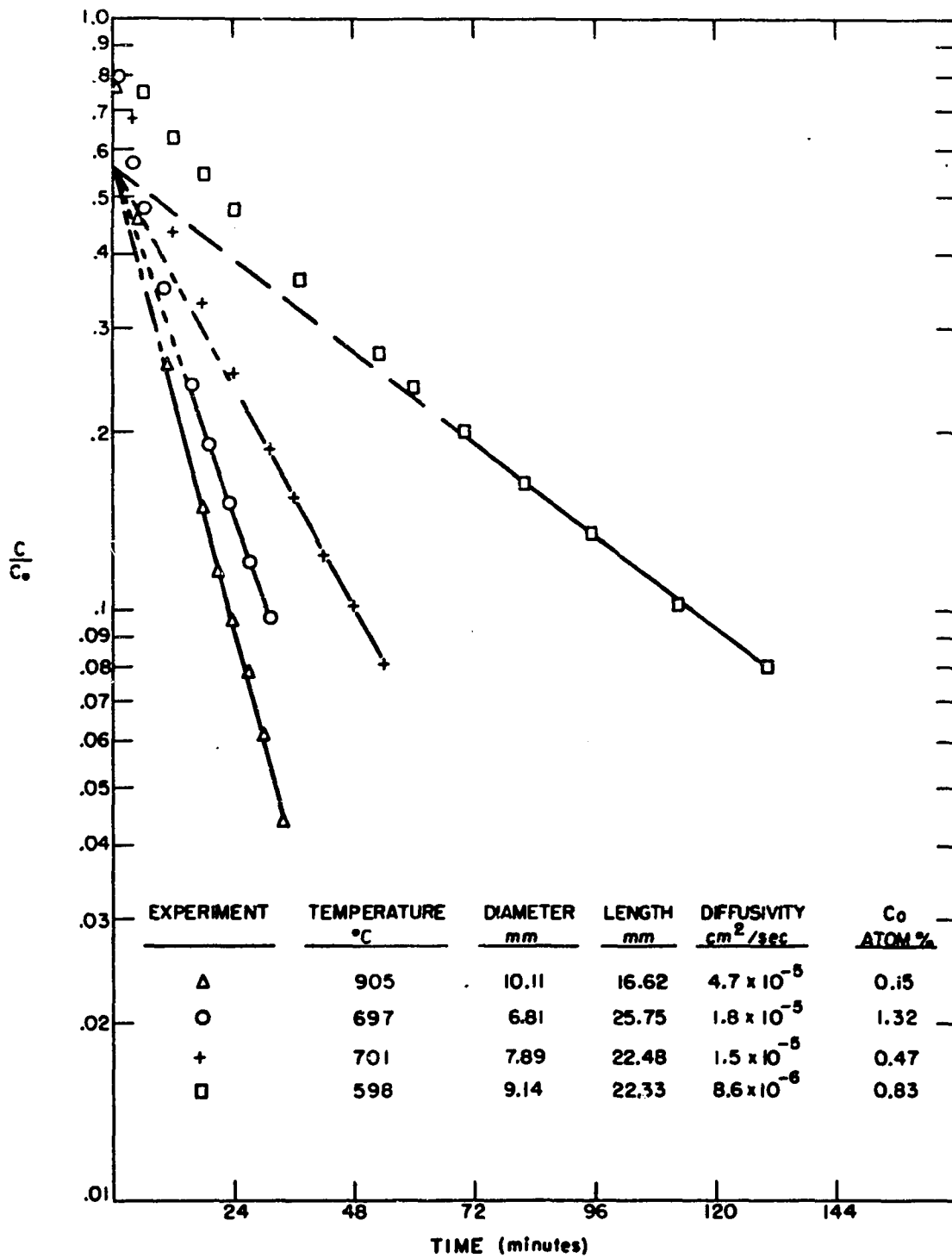
Figure 6. Evolution of hydrogen from thorium cylinders

EXPERIMENT	TEMPERATURE °C	DIAMETER mm	LENGTH mm	DIFFUSIVITY cm^2/sec	C_0 ATOM %
△	905	10.11	16.62	4.7×10^{-5}	0.15
○	697	6.81	25.75	1.8×10^{-5}	1.32
+	701	7.89	22.48	1.5×10^{-5}	0.47
□	598	9.14	22.33	8.6×10^{-6}	0.83

Table 4. Results of evolution rate experiments

Material	Temperature $^\circ$C	C_o atom percent	$D \times 10^5$ cm^2/sec
Swaged, annealed Ames Th	901	1.12	6.5
"	900	0.71	6.0
"	904	0.31	5.1
"	905	0.16	4.7
"	798	1.40	3.9
"	800	1.26	3.7
"	800	0.76	3.4
"	802	0.23	3.1
"	702	2.61	2.2
"	702	2.55	2.3
"	704	1.50	2.1
"	704	0.57	2.0
"	702	0.31	1.6
"	597	3.00	0.61
"	597	1.69	0.73
"	600	1.51	0.75
"	598	1.49	0.80
"	598	0.83	0.86
As cast Ames Th	798	0.29	2.7
Swaged, annealed crystal bar Th	901	0.88	5.7
"	901	0.34	5.0
"	701	1.06	1.9
"	701	0.47	1.5

four temperatures studied. The reason for the concentration dependence of the diffusion coefficient is not known. Plots of log D vs 1/T for $C_o > 0$ indicate that ΔH and D_o both increase with increasing initial hydrogen content. This behavior may be due, in part, to distortion of the thorium lattice caused by the presence of hydrogen. However, the
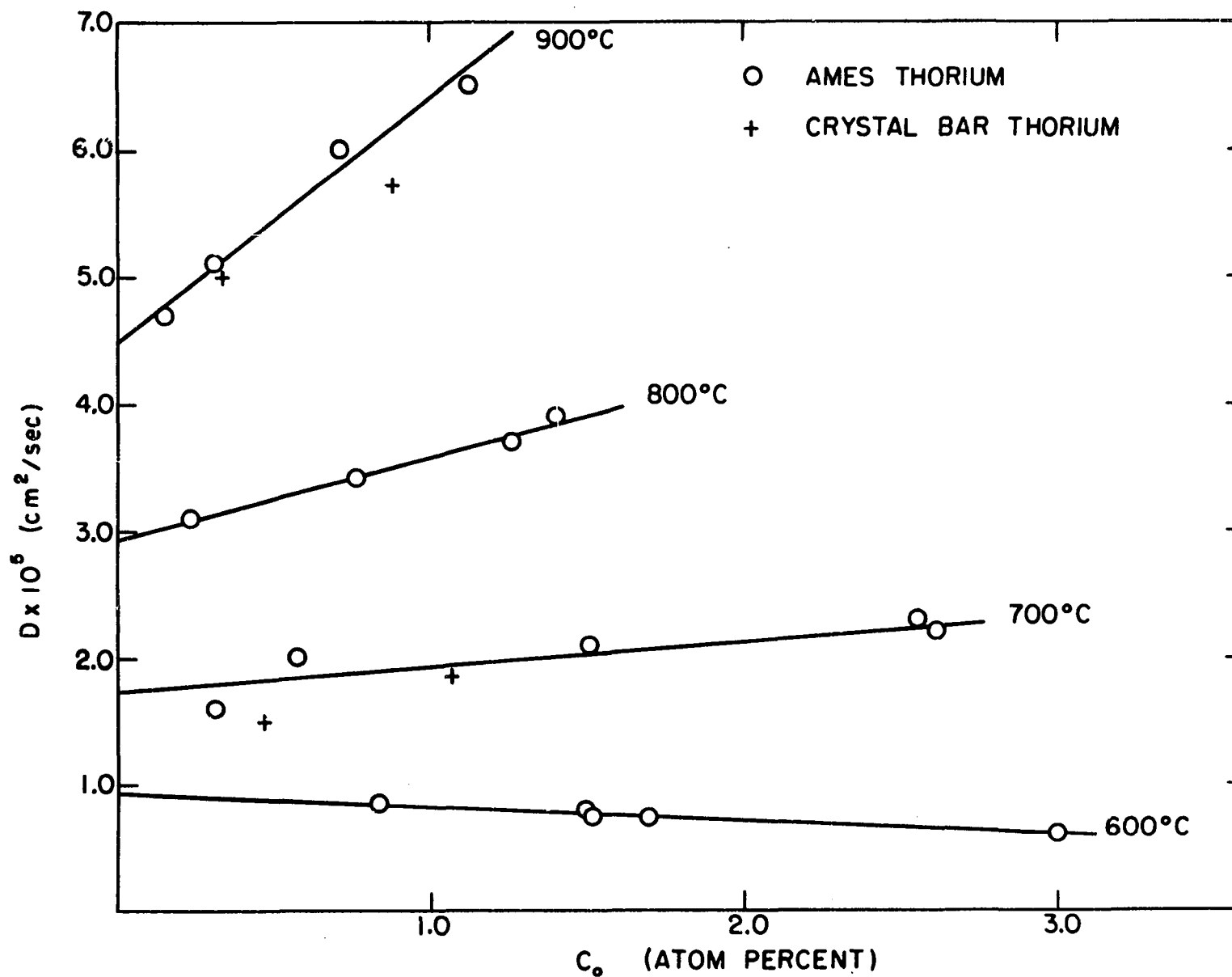
Figure 7. Variation of the diffusivity with initial hydrogen concentration

strain produced by interstitial hydrogen would probably be slight because of the small size of the hydrogen atom. Possibly a more likely cause would be interactions between the solute hydrogen atoms and crystal imperfections such as impurity atoms, dislocations and vacancies. Of the impurity atoms, carbon is the only one present in solution in numbers comparable to the number of hydrogen atoms in the specimens which were studied. Excellent evidence for the interaction of hydrogen and carbon atoms in thorium was found by Rexer (5). The fact that hydrogen hardens thorium (7) may indicate an interaction between hydrogen atoms and dislocations. Vacancies could be acceptors of hydrogen atoms or could have neighborhoods void of hydrogen. If the diffusivity of hydrogen atoms associated with an imperfection were different from that of hydrogen atoms in normal lattice positions and if the fraction of the total hydrogen which was associated with imperfections varied with composition, a concentration dependent diffusivity would be observed.

The log of D_n, the diffusivity extrapolated to zero hydrogen content, was plotted vs $10^3/T$. These points are shown as circles in Figure 8. The uncertainty in D_n is indicated by the length of the vertical line through each point. The linear plot indicates that

$$\log D_n = -2.535 - \frac{2134}{T} .$$
(17)

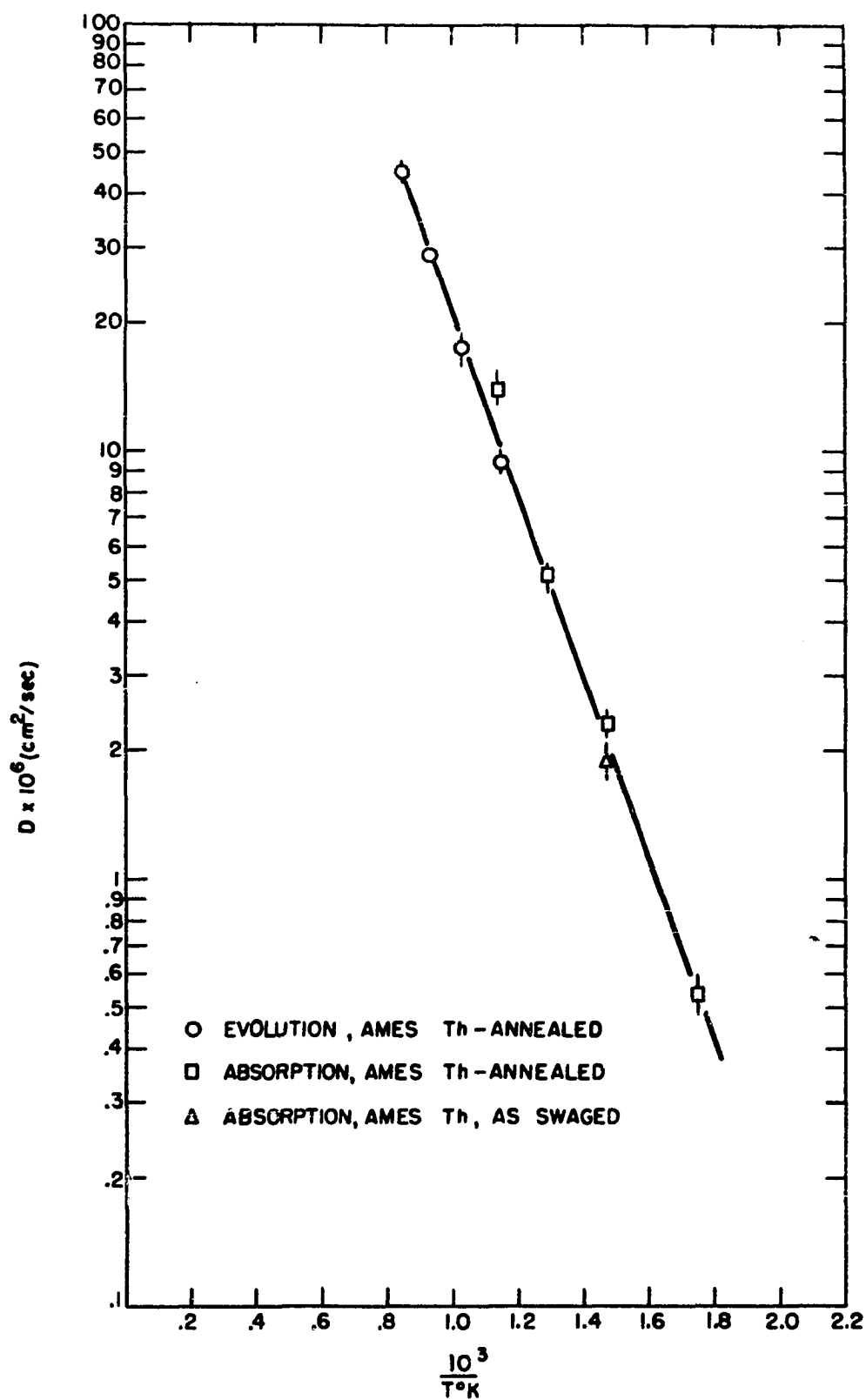Figure 8. Diffusivity of hydrogen in thorium

Therefore,

$$D_n = D_o e^{\frac{-\Delta H}{RT}} \qquad\qquad (18)$$

where

$$D_o = 2.92 \times 10^{-3} \text{ cm}^2/\text{sec}$$

$$\text{and } \Delta H = 9.75 \text{ kcal/g atom.}$$

Barrer (34) has enumerated some phenomena which can be rate controlling steps in the evolution and absorption processes. In the case of the evolution of hydrogen from a metal, the ion must diffuse to the surface, gain or lose an electron, combine with another atom, and escape from the surface, although the steps may not occur in that order.

In order to test whether the evolution rate was controlled by the diffusion of hydrogen in thorium or by some surface reaction, experiments were run with cylinders of various diameters. The surface to mass ratio of a cylinder can be shown to be proportional to $(\frac{1}{s} + \frac{1}{a})$, where a is the radius and s is the length of the cylinder. Therefore, for a long cylinder, the surface to mass ratio varies nearly inversely with a. Should the evolution rate be surface controlled, the evolution rate would vary nearly inversely with a. However, if diffusion is the rate controlling step, the evolution rate would vary nearly inversely with a^2, as seen in equation (9). The latter relationship was found experimentally, which strongly indicates that diffusion was the

rate controlling step in the evolution process.

The evolution rate was greatly affected if the surface was contaminated. If the pressure in the closed furnace system before a run was not constant and less than 10^{-5} mm of mercury, evolution of hydrogen from the cylinder occurred very slowly and the evolution curve never became linear. When this behavior was observed, the surface of the cooled cylinder always appeared noticeably darker than a freshly machined sample. The results of surface contamination were observed most frequently at and below 700°C. Below 600°C, no consistent results were obtained on any of the samples. Similar behavior has been noted for zirconium at 630°C and for titanium at 650°C (33). The upper temperature limit for this method was 900°C. At higher temperatures, evolution became too rapid to follow with the existing apparatus.

Figure 7 shows four points obtained using crystal bar thorium. While the values do not differ greatly from those for Ames thorium, they are consistently lower, possibly due to a minor influence of impurities on the diffusion rate. Grain boundary diffusion was not the major factor affecting the evolution rate but may have played a small part. The diffusivity for as-cast Ames thorium was found to be 2.7×10^{-5} cm^2/sec at 800°C compared to 3.1×10^{-5} cm^2/sec for the swaged and annealed Ames thorium. The as-cast material had a grain size of 25 grains per sq mm while the swaged and annealed

material had 2600 grains per sq mm.

2. Non-steady state absorption

The non-steady state absorption technique for determining the diffusivity of hydrogen in thorium was advantageous in that surface reactions could not be rate controlling, since the hydrogen gradient which was measured was entirely within the metal phase. The use of this method also increased the temperature range which could be studied. The time necessary for an experiment was prohibitively long below $300^O C$, and above $600^O C$ the quenching time was no longer negligible compared to the total time of the experiment.

Theoretical plots of $C-C_O/C_S-C_O$ vs r/a for diffusion into an infinitely long cylinder of uniform initial composition, C_O, are shown in Figure 9. Each curve is for a different value of Dt/a^2. The concentration of each section was assumed to be the concentration at a distance from the cylinder axis equal to the arithmetic mean of the inside and outside radii of the section. This mean distance was called r. The thickness of the hydride layer was assumed to be negligible for the calculations, since it was only about 2 percent of the radius of the cylinder. The validity of these assumptions has been shown by Mallett et al. (24). A typical set of experimental points for diffusion at $409^O C$ has been plotted in Figure 9. At each temperature, the value of C_S
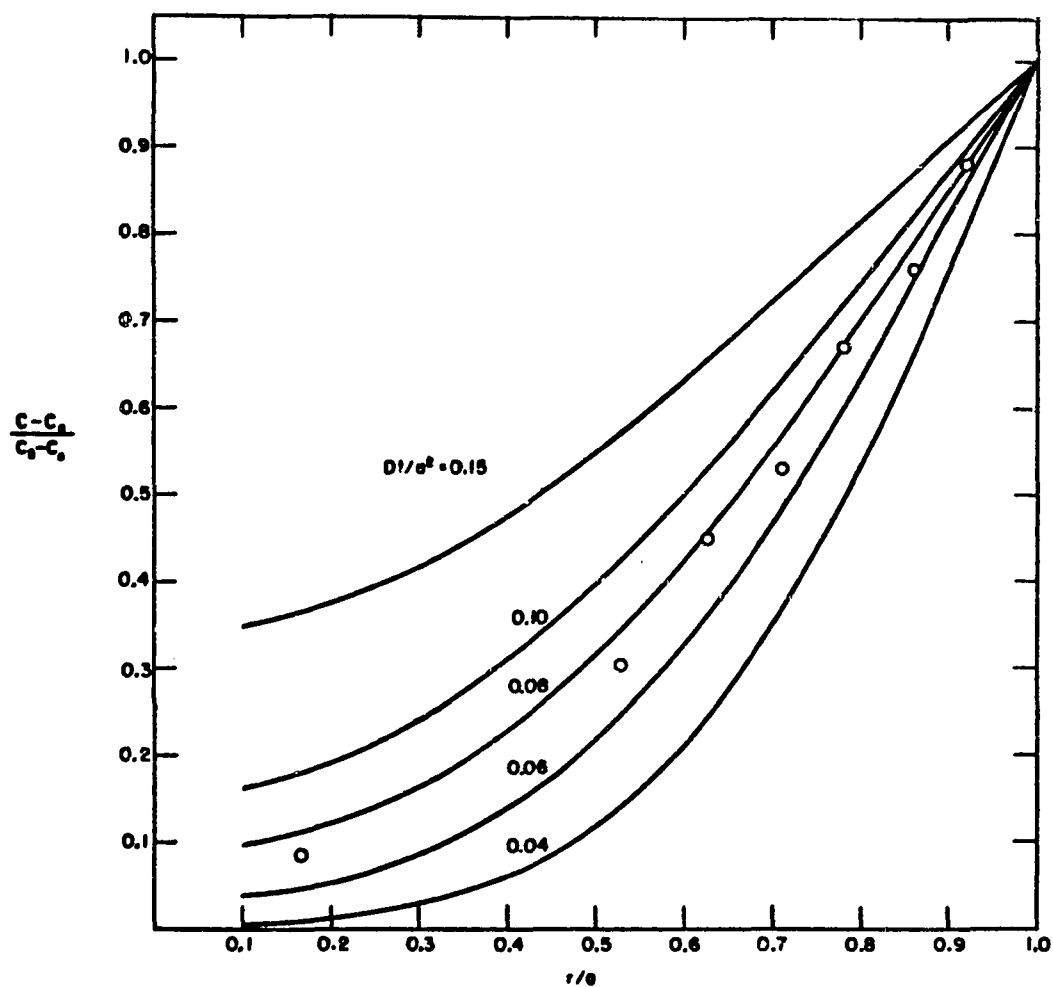
Figure 9. Experimental absorption data at 409°C with the theoretical absorption curves due to Carslaw and Jaeger (22)

necessary to make the experimental data fit the theoretical curves was less than the equilibrium solubility value found by Peterson and Westlake (6). This was to be expected since equilibrium did not exist at the thorium-thorium dihydride interface during the diffusion experiment.

The values of the diffusivity of hydrogen in swaged and annealed Ames thorium, found by the non-steady state absorption technique, are shown in Table 5 and have been plotted in Figure 8. Dt/a^2 can only be approximated to $\pm$ 0.005 from the theoretical absorption plots. The resulting uncertainty in D is indicated by the length of the vertical line through each square in Figure 8. Except for the value at $600^\circ C$, the points fall on the straight line through the values obtained by the evolution method. The high value obtained at $600^\circ C$ may be due to cooling too slowly. Since the total time of diffusion was only 15 minutes at this temperature, the time necessary to cool the sample inside the quartz tube under vacuum could be significant.

The fact that the values obtained by this method satisfy equation (17) even though they have not been extrapolated to zero hydrogen concentration is probably explained by the decrease in the solubility of hydrogen in thorium with decreasing temperature. The average hydrogen concentration of the metal phase is low at the lower temperatures, making D very little different from D_n.

Table 5. Diffusivities determined by the non-steady state absorption method

Material	Temperature ($^\circ$C)	C_s (atom percent)	Equilibrium[a] solubility (atom percent)	D (cm^2/sec)
Swaged and annealed Ames Th	602	9.0	12.0	$(1.4\pm0.1)\times10^{-5}$
"	504	5.5	7.6	$(5.2\pm0.4)\times10^{-6}$
"	409	2.3	4.3	$(2.3\pm0.2)\times10^{-6}$
"	298	0.9	1.7	$(5.4\pm0.6)\times10^{-7}$
Swaged Ames Th	408	2.3	4.3	$(1.9\pm0.2)\times10^{-6}$

[a]Peterson and Westlake (6).

The excellent linearity of the plot, in Figure 8, including both evolution and absorption data is further evidence that the evolution rates were diffusion controlled. Microstructure seemed to have little effect on the diffusion rate at $409^\circ C$. An absorption experiment using swaged Ames thorium without annealing gave a diffusivity of 1.9×10^{-6} cm^2/sec compared to 2.3×10^{-6} cm^2/sec for the annealed material.

IV. SUMMARY

The absorption rate of hydrogen by thorium has been
studied at temperatures between 350 and 700°C and pressures
up to 400 mm of mercury. Absorption followed the parabolic
rate law. Below 550°C, the log of the absorption rate varied
linearly with the reciprocal of the absolute temperature
making it possible to estimate the energy of activation for
diffusion of hydrogen in thorium dihydride to be 19.6 kcal.
The absorption rate showed no pressure dependence below 450°C.
At higher temperatures, the absorption rate increased with
increasing pressure. This pressure dependency became more
pronounced with increased temperature. Differences in the
purity level and the microstructure of the thorium metal
had only minor effects on the absorption rate.

The diffusivity of hydrogen in thorium was determined
at temperatures between 600 and 900°C by measuring the evolu-
tion rate of hydrogen from thorium cylinders. The value of
D found at a given temperature was dependent on the initial
hydrogen concentration of the cylinder. At 600°C, the dif-
fusivity decreased with increasing initial concentration,
while the opposite concentration dependence was observed at
and above 700°C. The diffusivities obtained by extrapola-
tion to zero concentration were plotted against $1/T$. The
linearity of this plot indicated that the temperature

dependence of the diffusivity of hydrogen in thorium
satisfies an Arrhenius equation, where D_o is 2.92×10^{-3}
cm^2/sec and the energy of activation for diffusion of hydro-
gen in thorium is 9.75 kcal/g atom. The evolution rate
varied nearly inversely with the square of the radius of
the sample which indicated that the rate controlling step
was diffusion. Had some surface reaction been controlling,
the evolution rate would have varied nearly inversely with
the radius. Graphical analysis of hydrogen concentration
gradient data, obtained from non-steady state absorption
experiments, gave values of the diffusivity at temperatures
between 300 and 600°C. These results, plotted as log D vs
1/T, fell on the same straight line as the evolution results.
This is further evidence that diffusion was the rate con-
trolling step in the evolution process. Differences in
microstructure and the purity level of the thorium had little
effect on the hydrogen diffusion rate.

V. BIBLIOGRAPHY

1. Gmelin, L., Handbuch der Anorganischen Chemie, System Nummer 44, Verlag Chemie, GMBH, Weinheim/Bergstrasse (1955).

2. Nottorf, R. W., Some problems in the chemistry of uranium and thorium of interest to the development of atomic power, Unpublished Ph. D. Thesis, Iowa State College Library, Ames, Iowa (1945).

3. Mallett, M. W., and I. E. Campbell, J. Am. Chem. Soc. 73, 4850 (1951).

4. Peterson, D. T., D. G. Westlake, and J. Rexer, The effect of thorium oxide on thorium-hydrogen equilibrium, Mimeo. report, Iowa State College Metallurgy Department, Ames, Iowa (1959).

5. Rexer, J., The effect of carbon on the thorium-thorium dihydride system, Unpublished M. S. Thesis, Iowa State College Library, Ames, Iowa (ca. 1959).

6. Peterson, D. T., and D. G. Westlake, Solubility of thorium dihydride in thorium metal. To be published in Trans. American Institute of Mining, Metallurgical, and Petroleum Engineers. (ca. 1959)

7. _____, Effect of hydrogen on tensile and impact properties of thorium. To be published in Proceedings of the Third Annual Reactive Metals Conference of the American Institute of Mining, Metallurgical, and Petroleum Engineers (ca. 1959)

8. Markowitz, J., and J. Belle, Thermal diffusion of hydrogen in zirconium, U. S. Atomic Energy Commission Report WAPD-TM-42 (Westinghouse Electric Corp.) (1957).

9. Shewmon, P. G., Trans. American Institute of Mining, Metallurgical, and Petroleum Engineers 212, 642 (1958).

10. Straetz, R. P., and J. E. Draley, A study of the reaction rate between thorium and purified hydrogen, U. S. Atomic Energy Commission Report CT-3045 (Chicago University Metallurgical Laboratory) (1945).

11. Belle, J., B. B. Cleland, and M. W. Mallett, J. Electro-chem. Soc. 101, 211 (1954).

12. Albrecht, W. M., and M. W. Mallett, J. Electrochem. Soc. 103, 404 (1956).

13. Gulbransen, E. A., Trans. Electrochem. Soc. 81, 327 (1942).

14. _____ and K. F. Andrew, J. Electrochem. Soc. 101, 348 (1954).

15. Wagener, S., Proc. Phys. Soc. B66, 400 (1953).

16. Gulbransen, E. A., and K. F. Andrew, J. Electrochem. Soc. 101, 560 (1954).

17. McGill, H. L., and W. L. Sibbitt, Diffusion of gases through metals, U. S. Atomic Energy Commission Report ANL-4603 (Argonne National Laboratory) (1951).

18. Davis, W. D., Solubility, determination, diffusion and mechanical effects of hydrogen in uranium, U. S. Atomic Energy Commission Report KAPL-1548 (Knolls Atomic Power Laboratory) (1956).

19. _____, Diffusion of hydrogen through poisoned palladium, U. S. Atomic Energy Commission Report KAPL-1375 (Knolls Atomic Power Laboratory) (1955).

20. Eichenauer, W., and A. Pebler, Z. für Metallkunde 48, 373 (1957).

21. Hill, M. L., and E. W. Johnson, Acta Met. 3, 566 (1955).

22. Carslaw, H. S., and J. C. Jaeger, Conduction of Heat in Solids, Oxford University Press, Oxford, England (1947).

23. Crank, J., Mathematics of Diffusion, Oxford University Press, Oxford, England (1956).

24. Mallett, M. W., E. M. Baroody, H. R. Nelson, and C. A. Papp, J. Electrochem. Soc. 100, 103 (1953).

25. _____ and W. M. Albrecht, J. Electrochem. Soc. 104, 142 (1957).

26. Wasilewski, R. J., and G. L. Kehl, Metallurgia 50, 225 (1954).

27. Barrer, R. M., Diffusion in and through Solids, Cambridge University Press, Cambridge, England (1941).

28. Geller, W., and T. H. Sun, Arch. Eisenhüttenwesen 21, 423 (1950).

29. Hill, M. L., and E. W. Johnson, Acta Met. 3, 99 (1955).

30. Demerez, A., A. G. Hock, and F. A. Meunier, Acta Met. 2, 214 (1954).

31. Gray, A., and T. M. Macrobert, A Treatise on Bessel Functions, Macmillan and Co., London, England (1922).

32. Griffith, C. B., and M. W. Mallett, Vacuum Metallurgy, Electrochemical Society, Inc., Baltimore, Maryland (1955).

33. Albrecht, W. M., and M. W. Mallett, Trans. American Institute of Mining, Metallurgical, and Petroleum Engineers 212, 204 (1958).

34. Barrer, R. M., Phil. Mag. (7) 28, 148 (1939).

VI. ACKNOWLEDGMENTS

The author is deeply grateful to Dr. David Peterson for his suggestions and advice which were always given in a manner encouraging initiative, self-expression and growth.

Thanks are also due Mr. Wayne Jones and Mr. Evert McKenna whose skill in glassblowing was invaluable during construction of the apparatus.

The author's wife, Helen, has been the inspiration for this work. Her understanding during the past four and one half years of graduate study has been immeasurable.