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The Magnesium-Hydrogen System

J. Frederick Stampfer Jr.

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Sept 23, 1958

The Magnesium-Hydrogen System

By

J. Frederick Stampfer, Jr.

A Dissertation

In Partial Fulfillment of the

Requirements for the Degree of

Doctor of Philosophy in Chemistry

The University of New Mexico

1958

This dissertation, directed and approved by the candidate's committee, has been accepted by the Graduate Committee of the University of New Mexico in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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INTRODUCTION

The motivating factor for this investigation of the magnesium-hydrogen system was the recent interest in the hydride of beryllium. Although beryllium hydride has been prepared by the pyrolysis of di-*t*-butylberyllium,¹ no evidence for the direct union of beryllium and hydrogen has been reported. It was thought that an examination of the reaction between magnesium and hydrogen and determination of the thermodynamic relations involved might have a bearing on this phenomenon. Also, the properties of magnesium hydride are interesting from an over-all periodic table viewpoint. The hydrides of beryllium and magnesium are usually considered to be intermediary between the saline, or ionic hydrides, and the metallic, or interstitial ones. It has been proposed that the structure of magnesium hydride might contain hydrogen bridges similar to those in the hydrides of boron and aluminum.² Although the physical properties have already been catalogued,³ this work has extended the data to higher pressures and temperatures.

Magnesium hydride has been prepared by a number of methods, chiefly by solution procedures (see History), but no detailed information as to the pressure-temperature-composition relationships from which the thermodynamic functions could be derived is available. Such information has been obtained in this investigation by the use of a suitable reactor and associated gas line and measuring apparatus to study the system at temperatures and pressures up to 600°C and 5000 p.s.i.

HISTORY

The first reported preparation of magnesium hydride, by Jolibois⁴ in 1912, utilized the thermal decomposition of ethyl magnesium iodide. In 1932 Zartman and Adkins⁵ reported the catalytic reduction of magnesium diphenyl with hydrogen over a nickel catalyst. Although there was no attempt to isolate magnesium hydride the amount of hydrogen absorbed was much greater than was required for the reduction of the hydrocarbon radical. Wiberg and Bauer⁶ in 1950, carried out the preparation by the pyrolysis of a magnesium dialkyl or a Grignard reagent. In 1951, Barbaras, Dillard, et al.,⁷ reported the preparation of magnesium hydride by the reaction of magnesium diethyl with lithium aluminum hydride. This method gave a white, non-volatile product which did not ignite spontaneously in air but reacted violently with water.

In 1951, Wiberg, Goeltzer, and Bauer⁸ reported the direct synthesis of magnesium hydride at 200 atmospheres and 540°C with magnesium iodide as a catalyst. This method resulted in a 60% yield of magnesium hydride. In 1955, Ellinger, Holley, et al.,³ again reported this preparation. They found no need for a catalyst under conditions less severe than those mentioned above. Moreover, the product was gray in color and much less reactive than the product prepared by the other methods; it decomposed slowly in water.

THEORY

A system of 2 components can exhibit either 1, 2, 3, or 4 phases. In the system under study, there are always at least two phases present: the gas phase and one or two solid phases. With just two phases (gas and one solid) the phase rule states that there are two degrees of freedom:

$$1) F = C - P + 2 = 2 - 2 + 2 = 2$$

F = degrees of freedom

C = components

P = phases

This means that if the pressure and temperature are fixed, the composition of the solid phase is established. In practice, if hydrogen is removed from the gas phase, thus lowering the pressure, the solid will evolve hydrogen and change its composition in accordance with Le Chatelier's principle.

If a second solid phase appears, there is only one degree of freedom. Thus, if hydrogen is removed at constant temperature, the pressure must remain constant as must the individual compositions of the two solids. However, the relative amounts of each phase will change with the one poorer in hydrogen increasing. In the following discussion the term "decomposition pressure", with no qualifying statements, will apply to the pressure over this two solid-phase region.

The actual species in these various solid phases are difficult to determine. However, if pure magnesium hydride was the starting material and if, when hydrogen were removed, there was still only one solid phase, then it would be logical to assume that the solid phase was magnesium hydride containing dissolved magnesium. Similarly, a one-solid phase region at the low hydrogen concentration end should consist of hydrogen and/or magnesium hydride dissolved in magnesium. These same two solid phases will be the ones present in the two-solid phase region. As hydrogen is removed, more hydride will decompose and the relative amounts of each phase will change until there is only the one, magnesium-rich, phase.

If the compositions of the phases in the two-solid phase region are magnesium saturated with hydrogen, magnesium hydride saturated with magnesium, and pure hydrogen, then the equilibrium reaction studied is

The standard free energy of formation represented by the equation

can be found by addition of the following reactions and corresponding equations for ΔF .

$$\text{Mg}(s, P_s) = \text{Mg}(\text{sat'd with H}_2, P \text{ eq}) \quad \Delta F = RT \ln \frac{a_{\text{Mg}}}{a_{\text{Mg}}^{\circ}}$$

$$\text{H}_2(f = 1) = \text{H}_2(P \text{ eq}) \quad \Delta F = RT \ln \frac{f_{\text{H}_2}}{f_{\text{H}_2}^{\circ}}$$

$$\text{MgH}_2(\text{sat'd with Mg, } P \text{ eq}) = \text{MgH}_2(s, P_s) \quad \Delta F = RT \ln \frac{a_{\text{MgH}_2}^{\circ}}{a_{\text{MgH}_2}}$$

$$\text{Mg}(s, P_s) + \text{H}_2(f = 1) = \text{MgH}_2(s, P_s) \quad \Delta F = \Delta F^{\circ} = RT \ln \frac{a_{\text{Mg}}^{\circ} f_{\text{H}_2}}{a_{\text{MgH}_2}}$$

$$\Delta F^{\circ} = RT \ln K, \text{ where } K = \text{equilibrium constant} = \frac{a_{\text{MgH}_2}^{\circ}}{a_{\text{Mg}}^{\circ} f_{\text{H}_2}}$$

a = activity of equilibrium components

a° = activity of materials in their standard states

f = fugacity of equilibrium components

f° = fugacity of materials in their standard states

$P \text{ eq}$ = pressure at equilibrium

P_s = standard state pressure, one atmosphere

It must be stated that the free energy change accompanying the change in pressure in going from $P = 1 \rightarrow P \text{ eq}$ for magnesium and magnesium hydride has been neglected as it can be shown, assuming no volume change in the materials, that it is less than 25 calories for the maximum pressure change.

It is shown in the experimental section that the hydrogen-rich phase is predominantly magnesium hydride so that the activity of this phase may be considered to be 1. If pure magnesium is taken as the standard state for the magnesium-rich phase and Raoult's law is assumed to hold for the magnesium in these solutions,

$$4) a_{Mg} = N_{Mg} \quad (N = \text{mole fraction}).$$

The thermodynamic functions can be calculated using the following relationships

$$5) \Delta F^\circ = -RT \ln K = -RT \ln \frac{1}{a_{Mg} f_{H_2}} = RT \ln N_{Mg} f_{H_2}$$

$$6) \Delta H^\circ = -T^2 \left(\frac{\partial (\frac{\Delta F^\circ}{T})}{\partial T} \right)_p$$

$$7) \Delta C_p^\circ = \left(\frac{\partial \Delta H^\circ}{\partial T} \right)_p$$

$$8) C_{pMgH_2}^\circ = \Delta C_p^\circ + C_{pMg}^\circ + C_{pH_2}^\circ$$

$$9) \Delta S^\circ = - \left(\frac{\partial (\frac{\Delta F^\circ}{T})}{\partial T} \right)_p$$

$$10) S_{MgH_2}^\circ = \Delta S^\circ + S_{Mg}^\circ + S_{H_2}^\circ$$

As shown in the errors section, the value of ΔF° calculated from equation 5 is, within experimental error, equal to the value calculated from

$$11) \Delta F^\circ = + RT \ln P_{H_2}$$

This is because a_{Mg} is slightly less than one and f_{H_2} is slightly greater than P_{H_2} , the two effects almost canceling each other. Consequently, we will use equation 11 as an empirical function to find the various thermodynamic values within the uncertainty of the experiment.

The expression for $\ln P$ as a function of temperature is given in the experimental summary section. It is of the form

$$\log P = A/T + B \log T + CT + DT^2 + E.$$

Applying this to equation 5

$$12) \Delta F^\circ = + 2.303 R (B T \log T + ET + CT^2 + DT^3 + A).$$

From equation 6

$$\Delta F^\circ/T + + 2.303 R (A/T + B \log T + CT + DT^2 + E)$$

$$- \frac{(\Delta F^\circ/T)}{T} = + 2.303 R (-A/T^2 + \frac{B}{2.303T} + 2DT + C) = -\Delta H^\circ/T^2$$

$$13) \Delta H^\circ = - 2.303 R (\frac{B}{2.303} + CT^2 + 2DT^3 - A).$$

ΔC_p° is calculated from equation 7 as,

$$14) \Delta C_p^\circ = - 2.303 R (2CT + 6DT^2 + \frac{B}{2.303}).$$

Equations for the heat capacities of magnesium and hydrogen are listed by Kelley⁹ in the form

$$15) C_p^\circ = F/T^2 + GT + I.$$

From equation 9, ΔS° is found to be

$$16) \Delta S^\circ = -2.303 R (B \log T + 2CT + 3DT^2 + \frac{B}{2.303} + E).$$

Equations for the entropies of magnesium and hydrogen are calculated from equation 15 by

$$S^\circ = \int \frac{C_p^\circ}{T} dT,$$

and are found to be of the form

$$17) S^\circ = F/T^2 + GT + I \ln T + J.$$

J may be evaluated by solving the above equation at 298.16°K and using the value for the entropy at that temperature given in the N.B.S. Circular No. 500.¹⁰

For the deuteride, the following heat capacity formula for deuterium was used:¹¹

$$C_p^\circ = 6.830 + 0.210 \times 10^{-3} T + 4.68 \times 10^{-2} T^2.$$

It was treated in the same manner as the equation for the heat capacity of hydrogen.

EXPERIMENTAL PROCEDURE

In general, the procedure consisted of loading a certain amount of magnesium or previously prepared magnesium hydride into a stainless steel reactor. The reactor is shown in Figure 2. This was then connected to a high pressure line (shown in Figure 1) and the contents allowed to react with hydrogen at the desired temperature and at a pressure at least double the decomposition pressure. As the amount of unreacted material decreased, the rate of reaction fell and the corresponding rate of pressure drop decreased, until it reached a limiting value. This was the rate of diffusion of hydrogen out of the reactor. At this point it was assumed that all of the magnesium which would react had been converted to the hydride.

Then, a portion of the hydrogen was allowed to pass from the reactor into the calibrated volume. (See Figure 1.) The actual amount of gas transferred was calculated from the increase in pressure in the calibrated volume. The change

in the amount of gas present in the gas phase of the reactor was calculated from its decrease in pressure. If this amount was smaller than that admitted to the calibrated volume, it was assumed that the solid phase had decomposed evolving an amount of gas equal to the difference in the two calculations. This process was continued through the decomposition pressure. In this region there were two solid phases present and large amounts of gas were evolved while the pressure remained relatively constant.

At low hydrogen concentrations, the evolution of gas from the solid phase was quite slow. The amount of hydrogen present in this region was determined from the pressure rise in the reactor after an aliquot of gas was removed. That is, hydrogen was removed, and the maximum subsequent pressure attained, corrected for diffusion, was noted. The quantity of hydrogen corresponding to this pressure rise was considered to be the difference in the equilibrium amounts present in the solid phase at the previous pressure (i.e., before removal), and the highest pressure actually recorded after the removal. By repeatedly removing gas, the total amount of gas in this one phase region could be determined.

The combination of this value with that for the hydrogen from the two phase region plus any from the one phase region of high hydrogen composition gave the total amount of hydrogen initially present in the magnesium. This value was a measure of the amount of magnesium hydride formed. All composition calculations were based on this value rather than on the amount of material originally loaded because there was a small variation in the amount of hydride formed in different runs. *

CHEMICALS

Magnesium

Three different sources of this material were used. The first of these, used in runs 1 through 4, consisted of fresh turnings made from a block of the doubly distilled material. Spectroscopic analysis showed a purity of 99.98% with the major impurities in ppm being: iron, 100; copper, 60; and zinc, 50. The oxide content was assumed to be very low as the turnings were prepared immediately before they were loaded into the reactor.

The second type, used in run 5, was magnesium pellets which had been procured in 1953 from Dow Chemical Co. Again, spectroscopic analysis showed a purity of greater than 99.9% with the main impurities being zinc, iron, and sodium. The oxide content did not appear to be greater than about 1% based upon the amount of hydrogen evolved when a sample was treated with acid.

The third type of material was magnesium hydride prepared by Metal Hydrides Inc., and was used in runs 6 and 7. The company analysis showed a hydride content of 93%. However, the material which was loaded into the reactor analyzed about 90% magnesium hydride.

Complete analysis of the third material utilized the following methods:

(1) spectrochemical, (2) X-ray, (3) optical, (4) combustion, and (5) solution.

(1) Spectrochemical analysis showed maximum metallic impurities to be less than 0.13%, with the major ones in ppm being: aluminum, 500; manganese, 300; iron, 200.

(2) In addition to magnesium hydride, the X-ray analysis indicated "about 10% Mg metal and a small proportion of MgO. The very fine crystal size of the MgO indicates that it probably formed at room temperature by decomposition of the hydride." ¹²

(3) Optical or microscopic examination showed "an estimated 10 to 15 percent of magnesium metal and only minute traces of magnesium oxide or magnesium hydroxide. The magnesium dihydride is present as single crystals and aggregates of crystals ranging from about 1 micron to over 500 microns across, although few grains exceed 300 microns across".¹³

(4) The combustion analysis consisted of passing oxygen over the heated hydride. Any hydrogen or carbon present would combine with the gas to form water or carbon dioxide, which was then absorbed in two previously weighed absorption tubes, one filled with magnesium perchlorate and the other with "Ascarite". The tubes were again weighed and values for the hydrogen and carbon present in the original sample obtained.

(5) In the solution analysis, samples of the hydride were treated with hydrochloric acid and the magnesium present determined chemically.

As more precise values for the weights of metallic magnesium and magnesium oxide had to be obtained than was possible by the X-ray or optical techniques, these were calculated from the amounts of hydrogen determined by combustion, and magnesium determined chemically. The applicable equations for the weights per gram of sample are as follows:

$$\text{weight MgH}_2 = \frac{26.34}{2.016} \left(\frac{\text{wt. H}_2}{100} \right)$$

$$\text{weight MgO} = \frac{40.32}{16} \left[1 - \frac{(\text{wt. H}_2 + \text{wt. Mg})}{100} \right]$$

$$\text{weight metallic Mg} = \frac{\text{wt. Mg}}{100} - \frac{24.32}{26.34} (\text{wt. MgH}_2) - \frac{24.32}{40.32} (\text{wt. MgO})$$

The final analysis shows:

Table 1

Analysis of Commercially Prepared Magnesium Hydride

<u>Component</u>	<u>Wt. %</u>	<u>Mole %</u>
MgH ₂	88.8	90.3
Mg	7.5	7.4
MgO	3.8	2.3

Hydrogen

Electrolytic, tank hydrogen was the source of the gas used. It was purified by passage, via 1/4" copper tubing, through an activated charcoal trap. All joints in the system were silver soldered except those on the trap itself which were welded. The trap was in the shape of a "U" made of 1" stainless steel tubing. Glass wool was inserted in the outlet side to prevent any carbon from being blown into the rest of the system.

A large mouth dewar was placed around the trap and filled with liquid nitrogen to cool the charcoal. The pressure was allowed to equilibrate with the tank at this temperature. Passage of the hydrogen into the rest of the system was delayed until the boiling of the liquid nitrogen was practically nil. It was then bled very slowly through the inlet valve. Analysis of the gas after passage through the carbon trap, showed a purity of greater than 99.94% with less than 0.01% water and the rest air.

The pressure in the high pressure system was raised above that in the tank by cooling the calibrated volume in liquid nitrogen and equilibrating it with the source. The inlet valve was then closed and the calibrated volume warmed.

Reactivation of the charcoal was accomplished by raising the temperature of the trap to 350 - 400°C under a vacuum of 1 μ or better. Joints on the vacuum system were soft soldered.

Deuterium

The deuterium used was treated in the same manner. Analysis of the gas showed 1.5 mole % hydrogen.

APPARATUS

High Pressure System (See Figure 1)

In this system only high pressure stainless steel tubing was used. Unless specified this was 1/4" x 0.083". Various valves were tried. These included 6,000, 15,000, 30,000, and 60,000 pound valves made by High Pressure Equipment Co., Autoclave Engineers, Inc., and American Instrument Co. All of these valves had revolving needle points which became galled after varying numbers of closures. To avoid this, valves with non-turning stems from Pressure Products Industries were used.

The system was designed with a minimum safety factor of six.

The various parts of this system will be described separately. The description is broken into sections based on those parts, the volumes of which were usually considered as a whole.

Calibrated Volume

A calibrated volume of approximately 30 ml. was fabricated from stainless steel by welding 1/4" thick bottoms and tops onto 1" x 3/4" tubing of the appropriate length. Pressure tubing was welded into the top and attached to a valve by means of a standard 1/4" jam fitting.

Figure 1
High Pressure System

HIGH PRESSURE SYSTEM

FIGURE 1

"X"

This part of the system, which had a total volume of about 4 ml. consisted of the following: 1) a high pressure cross; 2) three 2-way valves leading respectively to a pressure gauge, the vacuum system, and the source of H_2 ; 3) a 3-way valve which had one connection on the pressure side leading to the reactor.

The pressure gauge was a 5000 p.s.i. Heize gauge with 5 p.s.i. divisions. The first one used was 16" in diameter but after it developed a pin hole in the bourdon tube an 8" gauge was substituted, with no apparent loss in accuracy. To keep the useless volume as small as possible, the bourdon tube of the gauge was filled with mercury and a valve was added so that no mercury vapor would be introduced into the rest of the system when it was evacuated. One-eighth inch x 0.020" tubing was used to connect the valve and gauge. This, also, was to keep the volume small.

The connection to the vacuum system made possible the evacuation of the high pressure system without having to go through the charcoal trap.

Reactor and Measuring System

The design of this section took into account the following considerations. At elevated temperatures only part of the volume is in the hot zone resulting in a temperature gradient. As only the temperature extremes are known, the volume within this region (temperature gradient volume) should be small so that calculations of the amount of hydrogen present in the gas phase may be accurate. This necessitates tubing with a small inside diameter. A large inside diameter is needed so that gas transfer will be fast, especially while outgassing the

reactor. The outside diameter should be small so that heat conduction from the reactor will be kept to a minimum. As a compromise among these conflicting requirements, $1/8" \times 0.020"$ tubing was chosen.

To insure a measurable change in pressure from the dissociation of a small amount of magnesium hydride, the total volume of this system should be kept small, especially the cold zone. Still, it must be large with respect to the temperature gradient volume. Finally, the ratio of the volumes of the hot zone to the cold zone should be large so that changes in pressure, due to either changes in the amount of hydrogen present or to a change in the temperature of the reactor, will be measurable. A hot zone (reactor) volume of 5 - 7 ml and a cold zone ("T") of 2 - 3 ml were adopted.

For the purposes of description, this system will be broken down into it's two component parts.

"T". The Tee provided connections from the "X" to another pressure gauge and to the reactor. This gauge was the same kind as the original one in the "X" and it was treated in the same manner. Both were calibrated against a dead weight tester and were believed to be accurate within $\pm 1\%$.

Reactor. The designs of the various reactors took into consideration the following items.

As the temperature rises, the tensile strength of stainless steel falls markedly. Thus, calculation of wall thicknesses at the higher temperatures is important. Rupture in the tangential direction was assumed to be the most probable cause of failure. It was stress in this direction which was taken into account. This stress was calculated as follows:

$$S = \frac{P(b^2/a^2 + 1)}{(b^2/a^2 - 1)} \quad (1)$$

S = stress in tangential direction

P = internal pressure

b = outside radius

a = inside radius

For No. 347 stainless steel, which was used, the tensile strength at 650°C is 50,000 p.s.i. A safety factor of six means that the tensile stress should not exceed about 8,000 p.s.i. Solving equation (1),

$$b/a = \frac{S + P}{S - P}$$

Substituting 8000 p.s.i. for S and 5000 p.s.i. as the maximum internal pressure, b/a is calculated as 2. This ratio was equalled or exceeded at all times.

At first it was thought that welds might be a point of extra weakness. Because of this, the number of welds was kept to a minimum. Later, this precaution appeared to be unnecessary.

As temperatures were to be measured within $\pm 1^\circ\text{C}$, it was thought that a thermocouple well, with as thin walls as possible, should extend into the middle of the reactor volume. This was abandoned after a later reactor showed that there was no loss in accuracy when the thermocouple was placed in the reactor wall.

The main difficulty was caused by the many failures to find a suitable closure. One desirable feature was reuse of the reactor. As the temperature had to be cycled through hundreds of degrees, there was a good possibility that if metals of two different coefficients of thermal expansion were used they would

eventually pull apart and leak. For this reason, various jam fittings were tried. These all appeared to cause trouble by leaking, one only at high temperature. Permanently sealed closures were finally tried.

The various designs which were tried are described below.

1) The first had a $1/2$ " bore drilled in $1-1/8$ ", No. 310 stainless steel rod and was closed with a $1/2$ " jam fitting held on by a threaded cover. In the top of the $1/2$ " jam fitting was an $1/8$ " fitting which was used to attach the inlet tube. A $1/4$ " jam fitting was fabricated on the bottom of a thermocouple well, which extended the full length of the reactor bore, and fitted into a receptacle in the bottom of the reactor. On testing it was found that both the inlet tube and thermocouple fittings leaked so these were both welded shut. Trouble was also experienced with the large jam fitting which was finally tightened so much that it became welded in place on heating.

2) This reactor was fabricated from $1-1/2$ ", No. 347 stainless steel, hex stock. It had a $3/4$ " bore drilled from the bottom, with a $3/16$ " hole connecting to a $3/8$ " jam fitting. A $3/4$ " rod was turned down to form a bottom cover with a $1/4$ " x $1/8$ " thermocouple well which extended $3/4$ the length of the bore. This was welded to the bottom of the reactor. Another $1/8$ " well was drilled in the wall of the reactor. No temperature difference appeared between these two wells.

Into the top $3/8$ " fitting, $1/8$ " x 0.020" high pressure tubing was welded. This led out of the hot zone where hypodermic tubing was attached by silver soldering. This was to give some degree of flexibility when loading the reactor into the furnace.

Reactor 2 leaked at high temperatures.

3) A 1/2" bore was drilled, from the top, into 1-1/2", No. 347 stainless steel, hex stock. This was connected to the 1/8" inlet tube by a 2" long, 1/2" x 1/4" adapter. An 1/8" thermocouple well was drilled, from the top, into the reactor wall. After loading, the reactor was welded closed.

This reactor appeared to leak at high temperature. However, when helium was substituted for the hydrogen the pressure remained constant indicating that the loss of gas was actually due to diffusion rather than to a true leak. To determine through which part of the reactor most of the loss was taking place, the different sections of the reactor were fabricated separately and the loss from each measured.

4) With the assumption that the diffusion is inversely proportional to the wall thickness at constant temperature and pressure, a new reactor was designed which should have shown negligible diffusion. The body was a 3-1/2" long by 2" O.D. rod with a 2-3/4" x 1/2" bore. A 2" x 1-1/4" adapter with a 1/4" bore was welded into this. The inlet tube was attached by arc welding after loading with magnesium and cooling in liquid nitrogen.

The diffusion from this reactor was still much too high. There are four possible reasons why the actual rate of diffusion was greater than that calculated. a) One of the welds might have a thin spot; b) the assumption that the rate is inversely proportional to the wall thickness probably does not hold at these temperatures and pressures; c) different pieces of stock of the same type stainless steel (No. 347) may differ in their diffusion properties; d) the metal may change with use. That there was indeed a change with usage was shown by the

fact that the diffusion rates noted at different times but at the same temperatures and pressures were different. Photomicrographs of sections of the reactor also showed that some changes had taken place.

Which of these reasons is the most important is not known. However, in later runs, the welds appeared to have negligible effect and after the reactor was treated for hundreds of hours at elevated temperatures and pressures the diffusion rate was relatively reproducible.

5) The reactor which was finally used to obtain the data is shown in Figure 2. It was fabricated from a 7" length of 5" O.D. No. 347 stainless steel rod. A 1/2" hole, a, was drilled 4" deep through the bottom. A 1/4" neck, b, was drilled upwards another 2". Finally a 3/8" hole, c, was drilled from the top to meet the neck and the top tapped. A 2" x 1/2" plug, d, was pounded into the bottom of the large cavity so that it was flush with the bottom of the reactor and then welded in place. The top of the reactor was faced off leaving a 1/8" x 1/8" step, e, around the 3/8" hole. The neck was filled with a rod, f, held up by a flat head which was seated on the bottom of the 3/8" hole. A plug, g, was died to fit the 3/8" hole and extended 3/16" above the top of the 1/8" step. This plug had a 1/16" step, h, at the top around an 1/8" hole which was drilled through it. This step as well as the 1/8" one were to aid in the welding. An 1/8" inlet tube, i, was welded into the plug. Two thermocouple wells, j, were drilled parallel to and 1" from the neck and as deep as the top of the cavity.

The weld between the inlet tube and plug was first checked for leaks under vacuum. The starting material was then loaded into the reactor and the filler

Figure 2
Final Reactor Design

FINAL REACTOR DESIGN
FIGURE 2

rod inserted in the neck. Finally, the plug was screwed in and welded in place. The mass of the reactor body was so large that excessive heat did not reach the material in the cavity during welding.

To open the reactor, the inlet tube was broken off and the weld milled down until the remains of the plug could be removed. To reuse, the top of the reactor was faced off leaving another 1/8" step, the top of the hole retapped and a new plug made. In this way, the same reactor was reused 5 times. Before each use the cavity was cleaned with trichlorethylene, hot nitric acid, acetone, and water, and thoroughly dried at 100°C or more under vacuum.

Even in this heavy walled apparatus diffusion was still noticeable, although it was much smaller than in the other reactors. Also, the large mass of stainless steel dissolved appreciable amounts of hydrogen which were given off at lower (< 800 p.s.i.) pressures. However, by subjecting the empty reactor to runs similar to those in which magnesium was present, sufficient data were collected to correct for these effects. A discussion of these errors and the empty run is given in the section titled "Diffusion and Solubility".

Temperature, Production, Control and Measurement

The furnace proper (see Figure 3) consisted of an 18 ohm nichrome element, a, wrapped around an alundum tube, b, 5" in diameter and 11-1/2" high. This was surrounded with a 2" thick layer of asbestos, c, packed in a 17" high brass can with 1/8" thick walls, d. The bottom of the can was covered with fire brick, e. Inside the alundum tube was a 5" diameter x 1/16" thick brass can, f. The first 4 reactors were placed in a 5/8" thick copper jacket while the 5th just filled the furnace diameter. All were set on an alundum stand, g, on the bottom of the inner brass can. They were positioned slightly below the center of the furnace as heat loss out of the top should have been greater than out of the bottom. The

Figure 3

Furnace

FURNACE
FIGURE 3

top consisted of a transite lid, h, through which came the inlet tube and thermocouple leads from the reactor. On top of this was placed 4" of fiber glass insulation, i.

Pressures in this work were to be measured within temperature limits of $\pm 1^\circ\text{C}$. As equilibrium might be slow to be attained, the temperature had not only to be measured but controlled within these limits.

Temperature control was achieved, in part, by means of a Wheelco controller wired so that when the controller turned "off" the current would be reduced but not completely shut off. Both the "on" and "off" voltages could be varied. This arrangement was used to reduce the great variation in the temperature of the element and closely associated parts between the "on" and "off" positions. The element was a chromel-P alumel thermocouple, j, which was passed, via an alundum tube, k, through the insulation into the center of the furnace. The 1" air space between the element and copper shield of the first 4 reactors was to reduce temperature fluctuations. As there might be hot or cold areas within the furnace, the copper shield was used to attain the same temperature throughout the length of the reactor. With the 5th reactor, the great amount of stainless steel accomplished these same purposes. Through these precautions, temperature fluctuations were kept within $\pm 0.5^\circ\text{C}$. in the reactor. Also, there seemed to be no temperature difference within the reactor as shown by the two thermocouples.

Measurements were made by means of a Pt/Pt-10% Rh thermocouple. The cold junction ends were soft soldered to copper wire and set in a water-ice mixture. Measurements of the voltages produced were made with a Wenner potentiometer and a Rubicon galvanometer. Differences of 0.1 microvolt were registered with this system.

CALIBRATIONS

The standardized volume (C.V.) was calibrated by first weighing the empty cylinder and valve, and then filling with water and reweighing. This was accomplished by pulling a vacuum on the cylinder and then connecting it, by means of a 3-way stopcock, to a reservoir of water. After the volume had warmed to room temperature, the valve was closed and all the water was removed from around the stem. It was then reweighed. Difficulty was experienced in completely removing the water from around the stem which necessitated discarding the first 3 of 11 determinations. The final value obtained was 29.85 ± 0.01 ml.

The volume was then calculated as follows:

$$\text{Volume} = \frac{\text{weight of water}}{\text{density of water}}$$

$$\text{Weight of water} = \text{weight full-weight empty} + \text{weight of air in volume}$$

$$\text{Weight of air in volume} = \text{Volume} \times (\text{density of air})$$

$$\text{Volume} = \frac{\text{weight full} - \text{weight empty} + \text{Volume} \times (\text{density of air})}{\text{density of water}}$$

$$V = \frac{\text{weight full} - \text{weight empty}}{\text{density of water} - \text{density of air}}$$

$$V = \frac{29.85}{0.99768 - 9.3 \times 10^{-4}} = 29.95 \pm 0.01 \text{ ml.}$$

The error indicated is twice the standard deviation of the mean, as will be true with the following calibrations.

The calibration of the "X" was then accomplished by expanding helium or hydrogen gas into it from the calibrated volume (C.V.). The helium calculations were based on values of a and b from the International Critical Tables¹⁴ for the expression $PV = a + b(P)$ for one mole of gas.

For more than one mole

$PV = n[a + b(P)] = n f(P)$. This can be proved as follows:

P = pressure

V = volume

n = moles

d = density

$$P \frac{V}{n} = f(P) = \frac{P}{d}. \text{ If } n = 1 \text{ then } 1/d = V$$

and the expression is obviously true. However, if n is different from one then $1/d \neq V$. But, any value of d may also be obtained by assuming one mole of gas and a different volume - v' . Thus $1/d = V/n = \frac{v'}{1} = v'$,

$$P \frac{V}{n} = f(P) = P(1/d) = PV' = a + b(P)$$

$$\text{and } n = \frac{PV}{f(P)}.$$

To use this expression to determine unknown volumes the following method was used.

Let subscript 1 refer to the known volume before pressure equilibration.

Let subscript 2 refer to unknown volume before pressure equilibration.

Let subscript 3 refer to known plus unknown volume after pressure equilibration.

$$n_1 = \frac{P_1 V_1}{f(P_1)} \quad n_2 = \frac{P_2 V_2}{f(P_2)} \quad n_3 = \frac{P_3 V_3}{f(P_3)}$$

$$P_3 (V_1 + V_2) = (n_1 + n_2) f(P_3)$$

$$(V_1 + V_2) = \left[\frac{P_1 V_1}{f(P_1)} + \frac{P_2 V_2}{f(P_2)} \right] \frac{f(P_3)}{P_3}$$

$$V_1 + V_2 = V_1 \left[\frac{P_1 f(P_3)}{[f(P_1)](P_3)} \right] + V_2 \left[\frac{P_2 f(P_3)}{[f(P_2)](P_3)} \right]$$

$$V_2 \left[1 - \frac{P_2 f(P_3)}{[f(P_2)](P_3)} \right] = V_1 \left[\frac{P_1 f(P_3)}{[f(P_1)](P_3)} \right] - 1$$

$$V_2 = \frac{V_1 \frac{P_1 f(P_3)}{[f(P_1)](P_3)} - 1}{1 - \frac{P_2 f(P_3)}{[f(P_2)](P_3)}} = V_1 K$$

The hydrogen calculations, which appeared to be more accurate, were based on the d/d_0 values described in the P-V-T section. The derivation of the final equation

$$V = \frac{(d/d_0)_3 - (d/d_0)_2}{(d/d_0)_1 - (d/d_0)_3}$$

from the starting condition

$$n = K V (d/d_0)$$

is essentially the same as in the helium case and the subscripts have the same meanings.

The final calibration of the "X" was carried out with hydrogen. The volume was determined to be 4.75 ± 0.14 ml.

The "T" was calibrated by expanding gas into it from the "X" after placing a plug in the outlet. This volume was 2.31 ± 0.15 ml. After calibration, the plug was drilled and $1/8$ " tubing soldered into it. This was attached via a short length of hypodermic tubing to the inlet tube of the reactor. After loading with magnesium, the reactor was attached to the "T" and both calibrated. This was usually done with helium to avoid any reaction which might take place. With the commercial magnesium hydride,, however, hydrogen was used. The length of tubing

from the drilled plug to the top of the transite top of the furnace was measured and the volume of this cold zone calculated. This was added to the volume of the "T" which gave the total cold volume of the reactor system. The hot zone was the remainder.

CALCULATIONS

Pressure, Volume, and Temperature Relationships

Two different sets of calculations for the amount of hydrogen present in the gas phase were needed. The first were those under conditions at room temperature. These involved the calibrated volume, "X", and "T" as well as a few when the reactor was cooled. The other calculations were those in the hot zone of the reactor.

The most complete tabulation of P-V-T relationships which could be found was the National Bureau of Standards Circular No. 564 - Tables of Thermal Properties of Gases.¹⁵ This work compiled values of d/d_0 (a dimensionless representation of density related to the value at standard conditions) from 20 - 600°K and 0.01 - 100 atmospheres.

A table of differential values of d/d_0 with respect to temperature at constant pressure was made from which values up to 510°C were extrapolated. A large graph was then constructed of all these values from which the needed values of d/d_0 at specific temperatures and pressures could be found.

At 23°C, it was found that the second derivative of d/d_0 with respect to pressure was quite constant up to the maximum pressure tabulated, 100 atmospheres.

$$\frac{\Delta^2 (d/d_0)}{\Delta p^2} = 0.005.$$

For this reason, the extrapolation to pressures of 350 atmospheres was thought to be permissible.

At higher temperatures, neither the second derivative with respect to pressure nor temperature was constant. Thus it was decided that extrapolation could not be used. However, as the temperatures rises, the behavior of the gas approaches that of the ideal gas. Calculated compressibility factors, taken from High Pressure Technology by E. W. Comings,¹⁶ show a maximum deviation of 8% from ideality at the maximum pressure and the lowest temperature studied. As the actual calculations involve a change in pressure, the error is even less. During the removal of any one aliquot of hydrogen, the total calculated error should never exceed 3% and should almost always be less than 1-1/2%. For these reasons, the ideal gas law was used for the hot zone.

Experimental Calculations

When an aliquot of gas was removed from the reactor three quantities were determined. These were the changes in the amounts of gas in the "X", the cold and hot volumes of the reactor respectively. In the first two instances the following procedure was adopted:

- 1) Correction to change pressure reading to true pressure. The gauge error had been determined by calibration of the gauges against a dead weight tester. These corrections were been plotted vs. pressure and read therefrom for any pressure.

- 2) Conversion of p.s.i. to atmospheres. As the gauges were calibrated in p.s.i., this was changed to atmospheres by multiplying by 0.06805.

- 3) Determination of d/d_0 . These values were taken from the graph (described above) of d/d_0 vs. pressure at 23°C.

4) Calculation of amount of gas involved in pressure change. The two d/d_0 values were subtracted, converted to actual density, and multiplied by the volume. Thus:

$$\Delta n = \Delta(d/d_0) K V \quad K = 4.4586 \times 10^{-5} = \text{density of H}_2 \text{ at S.T.P.}$$

To calculate the number of moles transferred from the hot volume, steps 1 and 2 were the same, but at this point the change in pressure in atmospheres was found. This was multiplied by a factor which is equal to V/RT . That is, by the ideal gas law,

$$n = \frac{PV}{RT}$$

and

$$\Delta n = \Delta P V/RT$$

As an example, the actual calculations involved in the removal of the second aliquot in the determination of the 3rd isotherm at 510° from run No. 6 will be shown.

	"X"	Reactor
recorded pressure change p.s.i.	294 $\rightarrow$ 1065	2941 $\rightarrow$ 1939
corrected pressure p.s.i.	289 $\rightarrow$ 1056	2939 $\rightarrow$ 1936
changed to atmospheres	19.7 $\rightarrow$ 71.9	200.0 $\rightarrow$ 131.7 (hot volume)
d/d_0	17.9 $\rightarrow$ 63.5	163.3 $\rightarrow$ 112.0 (cold volume)
change in atmospheres		- 68.3 (-4.28 mmoles)
change in d/d_0	+ 45.6 (9.69 mmoles)	- 51.0 (-5.51 mmoles)
Total change in mmoles	+ 9.69 mmoles	- 9.79 mmoles

By adding the apparent amounts removed from the cold and hot volumes of the reactor system, the total amount of gas removed was found. This should be equal to or less than the amount introduced into the "X". As in this example, this was not the case for removals at high pressures.

As explained in the next section, one run was made with the empty reactor in which isotherms were taken at 510, 470, and 440°C. While the detailed results appear in that section, it should be noted here that at high pressures there appeared to be more gas removed from the reactor than appeared in the "X". Since this inconsistency was greater at higher pressures and lower temperatures, it would appear that the ideal gas law, used in the calculations pertaining to the hot volume, was more in error than the compressibility factors indicated. Another source of difficulty, which was more apparent at low pressures, was the solubility of hydrogen in the reactor. As the pressure was lowered, a part of the dissolved gas was evolved and this made it appear as if the solid phase were decomposing.

The sum of these effects was determined, by the empty run, and plotted against pressure for each of the three temperatures. When an aliquot of hydrogen was removed in a run with magnesium hydride, the suitable correction was found from the graph and applied.

In the above example, this amounted to 0.35 mmoles. Thus $9.69 + (-9.79 + 0.35) = 0.25$ mmoles of hydrogen were evolved from the solid phase.

DIFFUSION AND SOLUBILITY

As has been mentioned, diffusion was found to be a major consideration in the construction of the reactors. The final design reduced the loss of gas to such an extent that useful data could be collected. However, the exceedingly massive character of this reactor introduced the problem of hydrogen solubility in the stainless steel. To determine the extent of this effect so that it might be corrected for when necessary, a run was made with the empty container. Three isotherms were determined, at 510, 470, and 440°C, respectively.

When an aliquot of gas was removed from the reactor, four things were noted:

- 1) The amount of gas admitted to the "X". This was assumed to be the true amount removed from the reactor system.
- 2) The pressure immediately following the removal. If this pressure is used to calculate the amount of hydrogen removed from the reactor system, and if the P-V-T data are correct, then the calculation should show the same amount removed as was admitted to the "X". In reality, this was not the case due to the use of the ideal gas law. The difference in these two calculated amounts gives a measure of the actual correction required for this error.
- 3) The maximum pressure attained. The amount of gas required to raise the pressure from the initial value to the maximum value is the amount evolved from the reactor body. Figure 4 shows the sum of the needed corrections attributable to the use of the ideal gas law and the hydrogen dissolved in the reactor body for run No. 6 at 510°. These values are plotted assuming that at 90 p.s.i., approximately the lowest pressure reached in each isotherm, there was no hydrogen dissolved in the metal. This is, of course, not true

Figure 4

Sum of Corrections Attributable to Use of the Ideal Gas Law
and Hydrogen Dissolved in the Reactor Body for Run No. 6
and 510°

SUM OF CORRECTIONS ATTRIBUTABLE TO USE OF THE IDEAL GAS
LAW AND HYDROGEN DISSOLVED IN THE REACTOR BODY FOR
RUN NO.6 AND 510°.

FIGURE 4

but suffices for the present purpose. As the hot volume in any run was a function of the amounts of magnesium and magnesium hydride present, the actual volume was taken account of when making the corrections. The slight break in the curve is due to the change in volume when the magnesium hydride is converted to magnesium metal.

4) The rate of pressure drop, and thus the diffusion rate, after the maximum pressure had been attained. The data are quite incomplete due to the fact that the rates were not entirely reproducible. However, they were useful in determining whether the diffusion under any set of conditions was prohibitively high and if the material in the reactor had finished reacting.

EXPERIMENTAL

General

After the reactor was cleaned and dried by heating in vacuo, it was loaded with the starting material and closed by welding. The reactor was leak-tested using a Consolidated Electrodynamics Leak Detector Model 24-101A, first under vacuum and then, after attaching to the high pressure line, under pressure. If no leaks were found, the reactor was calibrated, heated to 500°, and, when magnesium was present, evacuated for a number of hours. When magnesium hydride was the starting material, this step was eliminated. Hydrogen was then added and allowed to react with any magnesium present.

Run No. 1

With the first few reactors, very little or no useful data were collected. In the run with reactor No. 3, however, the material remaining in the reactor was analyzed. The starting material was magnesium turnings. The final analysis

was accomplished by allowing the material to react with hydrochloric acid, measuring the amount of hydrogen given off, and having the final solution analyzed for total magnesium. The three possible products are: magnesium hydride, magnesium oxide, and magnesium metal. From the analysis, three quantities are known, i.e., sample weight, total hydrogen evolved, ($n_T H_2$), and total magnesium present ($n_T Mg$). Three equations can be set up with these knowns:

$$1) \text{ Sample weight} = 26.34 n_{MgH_2} + 40.32 n_{MgO} + 24.32 n_{Mg}$$

$$2) n_T H_2 = 2 n_{MgH_2} + n_{Mg}$$

$$3) n_T Mg = n_{MgH_2} + n_{MgO} + n_{Mg}$$

and if these equations are solved simultaneously, the following relationships are found:

$$n_{MgH_2} = \frac{16 n_T H_2 - 40.32 n_T Mg + \text{sample weight}}{18.02}$$

$$n_{MgO} = \frac{\text{Sample weight} - 24.32 n_T H_2 + 22.30 n_{MgH_2}}{40.32}$$

$$n_{Mg} = n_T Mg - n_{MgH_2} - n_{MgO}$$

where n is the number of moles.

The analysis showed a hydride content of 93.1 mole % and oxide and metal contents of 3.0 and 3.9% respectively.

Run No. 2

This run utilized reactor No. 4 and magnesium turnings. Although the diffusion rate was still too high for any composition data to be collected, a study was made of the decomposition pressure as a function of temperature.

[The text in this block is extremely faint and illegible, appearing as a series of horizontal lines across the page.]

About 130 points were taken at various compositions and at pressures of 34 p.s.i. to 4100 p.s.i. and temperatures of 314° to 576°. The data are tabulated in Table 2 and the curve drawn from them is shown in Figure 5. The equation which best fit this data was found to be

$$\log P = -4.090 \times 10^3/T - 2.441 \log T + 4.524 \times 10^{-3} T - 2.277 \times 10^{-6} T^2 + 13.214$$

where P is in atmospheres and T in °K.* As the reactor used in this run had the thermocouple closer to the reactants than in reactor No. 5, it was thought that the temperature corresponding to different decomposition pressures could be more closely determined than with the later reactor. For this reason, these values, and the equation derived from them, are assumed to be correct and in later runs the actual temperature of an isotherm was determined by the decomposition pressure. The thermocouples then showed any changes in temperature.

Because the diffusion rate was so high, a preliminary method to determine whether any one solid phase regions were present was possible. If the pressure in the reactor is raised above the decomposition pressure, and the temperature maintained constant, a plot of pressure vs. time could show the following characteristics. a) If it is assumed that the rate of diffusion at constant temperature remains constant, or decreases slowly and in a regular manner with decrease in internal pressure, then the first part of the graph should show a linear or slightly curved line with a negative slope. It should continue in this manner as long as diffusion is the only important process taking place;

* We would like to express our appreciation to Group T-1 of the Los Alamos Scientific Laboratory for solving this problem on an IBM Data Processing Machine No. 704.

Table 2
Experimentally Determined
Decomposition Pressures of MgH_2 and MgD_2

MgH_2						MgD_2			
Temperature °C	Pressure p.s.i.	Temperature °C	Pressure p.s.i.	Temperature °C	Pressure p.s.i.	Temperature °C	Pressure p.s.i.	Temperature °C	Pressure p.s.i.
314	34	415	344	480	1094	571	3910	305	29
330	54	417	366	483	1156	571	3919	330	66
334	54	418	368	489	1273	571	3918	359	116
334	59	420	386	490	1282	571	3913	380	227
335	56	423	405	491	1296	571	3896	409	402
335	60	427	450	491	1337	571	3897	461	1007
336	61	427	442	491	1306	571	3892	480	1383
336	64	429	461	491	1313	571	3901	492	1655
336	59	431	471	493	1472	571	3895	503	1955
349	85	433	488	494	1371	571	3890	510	2160
352	86	433	488	495	1401	571	3898	532	2938
355	103	435	534	497	1445	572	3896	561	4247
359	101	437	554	501	1518	575	4104		
365	133	441	566	504	1577	575	4111		
370	134	444	602	504	1582	575	4114		
370	140	444	646	504	1580	575	4097		
372	133	446	622	508	1669	575	4106		
373	144	448	640	509	1710	575	4090		
377	159	448	662	510	1720	575	4122		
377	161	449	655	511	1752	576	4125		
379	172	451	676	515	1857	576			
379	165	453	703	515	1866				
382	179	455	782	516	1838				
385	196	457	792	517	1786				
386	193	457	756	520	2007				
389	201	461	826	523	2087				
392	220	462	846	526	2156				
393	217	465	871	531	2331				
394	242	466	885	539	2608				
395	229	466	913	540	2615				
397	248	468	913	561	3425				
398	249	469	927	571	3898				
403	272	469	929	571	3906				
404	275	470	950	571	3907				
406	293	475	1015	571	3904				
407	296	479	1094	571	3905				
					3902

Figure 5

Experimental Decomposition Pressure

FIGURE 5

100

50

0

50

100

150

200

250

300

350

400

450

that is, there is no decomposition of the solid. b) Whenever the solid composition begins to change, the curve should show a discontinuity in the slope. If it remains a single phase, however, a decrease in pressure with time should still be seen. c) In the region where the solid consists of two phases, the curve should be horizontal at constant pressure. d) Below the 2 phase region, the pressure should again drop with any sudden change in composition again shown by a discontinuity in the slope.

In actuality, the beginning of the curve showed a slight curvature but no discontinuity was seen until a second solid phase appeared. In the region indicated by d above, the curve was smooth until there was evidence of a discontinuity about 300 - 400 p.s.i. below the decomposition pressure. Thus there was no solid solution at the high hydrogen composition end but there was some below the decomposition pressure.

Run No. 3

This run, and all subsequent runs, utilized reactor No. 5 and, in this case, 27.95 mmoles magnesium turnings. Although this run included the determination of 25 isotherms, the results were inconclusive because mercury appeared in the product. This material was used to fill the gauges and some of it must have been jarred from one of them and swept into the reactor as hydrogen was added. It appeared, in retrospect, that the magnesium amalgams which were produced were more stable than the magnesium hydride, as at one time the pressure of the hydrogen rose in the reactor shortly after the mercury could have been introduced and when there was hydride present. Also, in the 20 isotherms at 510°,

the amount of hydrogen taken up varied from 20.2 to 26.6 mmoles. However, as the amount of hydride formed did not steadily decrease, but rather varied unevenly from time to time, the mercury must have slowly distilled from the reactor and have been periodically replaced.

Although the mercury invalidated any final conclusions as to the shape of the isotherms, the results agreed closely enough with those finally found in a clean system that the results will be briefly noted. First, it should again be mentioned that composition calculations were based on the total amount of hydrogen withdrawn from the solid rather than on the amount of magnesium originally loaded.

The composite 510° isotherm exhibited less than 1/2% solid solution at the high hydrogen composition end. That is, any solid solution would have had to exist at compositions greater than $\text{MgH}_{1.99}$. The two solid phase region existed for about 95% of the total range. Immediately below this, the pressure fell rapidly with no sign of solid decomposition until at about 500 p.s.i. below the decomposition pressure, hydrogen was again evolved from the solid. Relatively large amounts of hydrogen were evolved in the first 100 p.s.i. pressure drop, but after this smaller amounts were given off down to 200 p.s.i. when the isotherms were discontinued. About 4-1/2% of the total hydrogen was given off in this region. This isotherm is shown in Figure 6.

The isotherms at the other two temperatures, 440 and 470°, were not as carefully studied, especially at the low pressure end. However, the data which were collected appeared quite similar to the 510° data.

Figure 6

510° Isotherms of Runs No. 3 and 6

510° ISOTHERMS OF RUNS NO. 3 AND 6

FIGURE 6

Runs No. 4 and 5

In the first of these runs, magnesium turnings from a new block of the doubly distilled material were used; while in the second, magnesium pellets obtained from Dow Chemical in 1953 were used. In neither case was it possible to change all the magnesium to magnesium hydride. The results appear below in Table 3 and it can be seen that the amount of magnesium hydride did not necessarily increase with the length of time of the reaction, the pressure of the reaction, or with the total number of times that magnesium hydride was formed. All data were taken at 510°.

Table 3

Reaction Conditions for runs No. 4 and 5

<u>Number</u>	<u>Time of reaction (hours)</u>	<u>Pressure of reaction (p.s.i.)</u>	<u>% of total magnesium hydrided</u>
Run No. 4. 51 mmoles magnesium were loaded.			
a	17	4000 - 3000	62
b	49-1/2	4500 - 4000	79
c	66-1/2	4500 - 3000	72
Run No. 5. 274 mmoles magnesium were loaded.			
a	45	4000 - 2000	38
b	69	4500 - 3000	29

Run No. 6

In this run, 4.3790 grams of magnesium hydride (161.1 mmoles of magnesium) from Metal Hydrides Inc. were used.

As the reactor was warmed, decomposition pressures over the material were measured at five different temperatures. These pressures all agreed closely with those found in run No. 2.

Four isotherms were carried out at 510°, and one each at 470° and 440°C. Each of these was carried to a minimum pressure of about 200 p.s.i. at which point it was impossible to decide whether the hydrogen liberated was coming from the reactor or the magnesium. The important data are listed below in Table 4.

As can be noted, there seems to have been very little solid solution at the high hydrogen concentration end. However, the amount is so small it falls within the experimental error. The total amount of magnesium hydride formed is of fairly constant value in the first five isotherms. The 440° isotherm shows less hydride formation, possibly due to the lower temperature of reaction. The extent of the lower one phase region also appears less but this may be due to stopping the isotherm at 200 p.s.i. The individual isotherms are shown in Figures 6 and 7.

The reactor was opened after the 440° isotherm so that no chemical analysis of the hydride was possible.

Run No. 7

In this run 4.4663 grams magnesium hydride (164.3 mmols magnesium) were used as the starting material. This time excess hydrogen pressure was kept over the material while the reactor was heated. Three isotherms were run; one each at 505° and 560° with hydrogen, and one at 510° with deuterium. The results are shown in Table 5 and Figure 8. Finally, the material was allowed to react again with deuterium and the resulting product removed for analysis.

Table 4

Results of run No. 6

<u>Isotherm</u>	<u>Temperature of reaction °C</u>	<u>Time of reaction (hours)</u>	<u>Pressure of reaction (p.s.i.)</u>	<u>% Mg hydrided</u>	<u>% H₂ in upper 1-phase region</u>	<u>% H₂ in 2-phase region</u>	<u>% H₂ in lower 1-phase region</u>	<u>Composition at end of 2-phase region x in MgH_x</u>
510-a	510	18-1/2	4500 - 4400	93.3	0.2	98.6	1.2	0.024
510-b	510	65	4500 - 4200	93.4	0.2	97.8	2.0	0.040
510-c	510	46-1/2	4700 - 4100	92.6	0.4	97.9	1.7	0.034
510-d	510	140-1/2	4500 - 4000	95.5	0.5	97.7	1.8	0.036
470	510	90-1/2	4600 - 4200	92.1	0.2	98.3	1.6	0.032
440	470	95	4600 - 4000	90.2	0.4	98.6	1.0	0.020

Table 5

Results of run No. 7

<u>Isotherm</u>	<u>Temperature of reaction °C</u>	<u>Time of reaction (hours)</u>	<u>Pressure of reaction (p.s.i.)</u>	<u>% Mg hydrided</u>	<u>% H₂ in upper 1-phase region</u>	<u>% H₂ in 2-phase region</u>	<u>% H₂ in lower 1-phase region</u>	<u>Composition at end of 2-phase region x in MgH_x</u>
505-H ₂	510	46	4500 - 3900	94.4	0.0	98.7	1.3	0.026
560-H ₂	540, 560	72	4800 - 4500	94.1	0.7	94.2	5.1	0.102
510-D ₂	510	94	4400 - 3600	92.0	0.2	97.4	2.4	0.048

Figure 7

440° and 470° Isotherms of Run No. 6

440° AND 470° ISOTHERMS OF RUN NO.6

FIGURE 7

Figure 8
Isotherms of Run No. 7

FIGURE 8

The first 505° isotherm appeared, in general, to be similar to those of run No. 6. However, the decomposition pressure seemed to fall as the lower limit of the two phase region was approached. This apparent drop was probably caused by not allowing the pressure to come to equilibrium after withdrawing an aliquot of hydrogen. The decomposition of the solid seemed to be much slower than was noticed in any other run, and thus the pressure approached equilibrium much more slowly. The reason for this behavior is not clear, but it may be a type of "hysteresis" effect, as this was the first time this particular material was decomposed. The corresponding isotherm in run No. 6 would not have shown this behavior as the last aliquot of hydrogen removed from the two phase region was relatively large and the final pressure was far below the decomposition pressure.

For the isotherm at 560°, the magnesium was allowed to react with hydrogen at 540° for 51 hours and 21 hours at 560°. The reason for the lower temperature for the major part of the reaction time was because of the high rate of diffusion at 560°. Since there was no run with the empty reactor at this temperature, the composition calculations were slightly less accurate than for the isotherms at lower temperatures. The results were quite similar to those of the other isotherms except there was more solid solution at the lower composition end. This amounted to 5.1% of the total hydrogen.

After completion of this isotherm, the reactor was evacuated for half an hour, about half the requisite amount of deuterium to form magnesium deuteride was added, and the decomposition pressure at eleven different temperatures

determined. After adding 2° to each of the recorded temperatures, to correct for the temperature differences due to the larger reactor used in this run, these few points, listed in Table 2, were treated in the same manner as all the hydride points. While the calculated equation fit the experimental points well, subsequent calculations of ΔS and ΔC_p at 298.16°K gave impossible values. Since there were so few values, and because a straight line fit the points in a $\log P$ vs. $1/T$ plot fairly well, it was decided to use the following equation to express the decomposition pressure as a function of temperature:

$$\log P = - \frac{4.00 \times 10^3}{T} + 7.26$$

The curve of the experimentally determined values is shown in Figure 5.

After allowing the rest of the magnesium to react with deuterium, an isotherm was taken. This isotherm exhibited slightly more solid solution at the low hydrogen end of the composition range than did the 510° hydride isotherms.

Finally, the deuteride was formed again and, after opening, a sample was subjected to X-ray analysis. The results of this were as follows. "In addition to the MgD_2 this sample contains appreciable MgO , an estimated 5% Mg metal, perhaps a few per cent of Mg_2Si and very small proportions of apparently two unidentified materials.

The lattice constants of the tetragonal unit cell of the MgD_2 were found to be

$$a = 4.5024 \pm 0.0005 \text{ \AA}$$

$$c = 3.0123 \pm 0.0005$$

The calculated density is 1.542 g/cm^3 .¹⁷

Combustion and solution analyses showed 79.9% MgD_2 , 5.2% Mg, 7.0% MgO , and 7.9% MgH_2 . Since no separate magnesium hydride phase was found by X-ray analysis the hydrogen was presumably dissolved in the magnesium deuteride lattice.

ERRORS

The following are the estimated errors in the experimentally determined quantities

Temperature $\pm 2^\circ$

Pressure

Reactor gauge ± 5 p.s.i.

C. V. gauge ± 2 p.s.i.

Volume

C. V. 29.95 ± 0.01 ml.

"X" 4.75 ± 0.14 ml.

"X" + C.V. 34.70 ± 0.14 ml.

Cold Volume of reactor system 2.31 ± 0.15 ml.

Hot Volume of reactor system 6.44 ± 0.15 ml.

Two sets of error calculations were needed. The first were those referring to the compositions, while the second were the errors associated with the calculated thermodynamic quantities.

Composition

The composition at any point was expressed by

$$1) \quad x \text{ in } \text{MgH}_x = 2\left(\frac{\Delta'n}{\Delta n_T}\right)$$

Δn_T = total hydrogen removable from solid phases

$\Delta'n$ = hydrogen remaining in solid phases.

The error in x is given by,

$$2) \quad \epsilon_x = 2\left(\frac{1}{\Delta n_T}\right)^2 \sqrt{(\Delta n_T)^2 \epsilon^2 \Delta' n + (\Delta' n)^2 \epsilon^2 \Delta n_T}$$

ϵ = error

For the calculation of these errors, three assumptions were made. The first was that the gases obeyed the ideal gas law. Although this was not true, it was satisfactory for the purpose. Thus

$$3) \quad \Delta n = H_2 \text{ evolved from solid} = 1/RT(\Delta P_X V_X - \Delta P_T V_T - \Delta P_R V_R)$$

where the subscripts X , T , and R refer to the "X" (or "X" + C.V.), cold volume and hot volume of reactor system respectively,

ΔP = pressure change

and

V = volume.

The error in Δn , $\epsilon_{\Delta n}$, is derived as follows.

$$\left(\frac{\epsilon_{\Delta n}}{\Delta n}\right)^2 = \left(\frac{\epsilon_T}{T}\right)^2 + \left(\frac{\epsilon_Z}{Z}\right)^2 \quad \text{where } Z = (\Delta P_X V_X - \Delta P_T V_T - \Delta P_R V_R).$$

Assuming that the temperature error is negligible compared to the pressure-volume error,

$$\begin{aligned} \left(\frac{\epsilon_{\Delta n}}{\Delta n}\right)^2 &= \left(\frac{\epsilon_Z}{Z}\right)^2 \\ \epsilon_{\Delta n} &= \Delta n \sqrt{\left(\frac{\epsilon_Z}{Z}\right)^2} \end{aligned}$$

But as $\Delta n = 1/RT (Z)$

$$\epsilon_{\Delta n} = 1/RT \sqrt{(\epsilon_Z)^2}$$

$$\epsilon_Z^2 = \sum \epsilon_{\Delta PV}^2 \quad \text{and} \quad \epsilon_{\Delta PV}^2 = (\Delta PV)^2 \left[\left(\frac{\epsilon_{\Delta P}}{\Delta P} \right)^2 + \left(\frac{\epsilon_V}{V} \right)^2 \right].$$

Thus,

$$4) \quad \epsilon_{\Delta n} = 1/RT \sqrt{(\Delta P_X V_X)^2 \left[\left(\frac{\epsilon_{\Delta P_X}}{\Delta P_X} \right)^2 + \left(\frac{\epsilon_{V_X}}{V_X} \right)^2 \right] + (\Delta P_T V_T)^2 \left[\left(\frac{\epsilon_{\Delta P_T}}{\Delta P_T} \right)^2 + \left(\frac{\epsilon_{V_T}}{V_T} \right)^2 \right] + (\Delta P_R V_R)^2 \left[\left(\frac{\epsilon_{\Delta P_R}}{\Delta P_R} \right)^2 + \left(\frac{\epsilon_{V_R}}{V_R} \right)^2 \right]}.$$

The second assumption was that there was no solid solution at the high hydrogen concentration end of the composition range. Therefore,

$$5) \quad \Delta n_T = \Delta n_{2 \text{ phase}} + \Delta n_{1 \text{ phase}}$$

It should also be noted that the error calculations were based upon a hypothetical isotherm run at 510°. Since the calculated error was a function of the number of aliquots of hydrogen removed, and the pressure drop accompanying each removal, an "average" isotherm was used. In the two solid phase region this isotherm consisted of 1 removal of gas from the reactor into the "X" + C.V. with an accompanying 1100 lb. rise and 6 aliquots admitted to the "X" only with a corresponding 500 lb. pressure rise. In the 1 phase region, 9 removals were assumed each accompanied by 150 lb. pressure changes in the "X", cold volume and hot volume. This "average" is a composite of all the 510° isotherms.

The total error in Δn_T is

$$6) \quad \epsilon_{\Delta n_T} = \sqrt{\epsilon_{\Delta n_{2 \text{ phase}}}^2 + \epsilon_{\Delta n_{1 \text{ phase}}}^2}$$

$$7) \quad \epsilon_{\Delta n_{2 \text{ phase}}} = \sqrt{\epsilon_{\Delta n_X + C.V.}^2 + 6\epsilon_{\Delta n_X}^2}$$

As the pressure drop in the reactor system is quite small in the 2 phase region, the last 4 terms in eq. 4 can be dropped. Thus,

$$\begin{aligned} 8) \quad \epsilon_{\Delta n_{2 \text{ phase}} (X + C.V.)} &= \Delta n_X + C.V. \sqrt{\left(\frac{(\Delta P)_X + C.V.}{\Delta P_X + C.V.}\right)^2 + \left(\frac{\epsilon_{V_X + C.V.}}{V_X + C.V.}\right)^2} \\ &= 107.3 \sqrt{\left(\frac{4}{1100}\right)^2 + \left(\frac{0.14}{34.7}\right)^2} \\ &= 107.3 (0.0057) \\ &= 0.61 \text{ mmoles} \end{aligned}$$

$$\begin{aligned} 9) \quad \epsilon_{\Delta n_{2 \text{ phase } X}} &= \Delta n_X \sqrt{\left(\frac{(\Delta P)_X}{\Delta P_X}\right)^2 + \left(\frac{\epsilon_{V_X}}{V_X}\right)^2} \\ &= 6.7 \sqrt{\left(\frac{4}{500}\right)^2 + \left(\frac{0.14}{4.75}\right)^2} \\ &= 6.7 (0.03) \\ &= 0.20 \text{ mmoles} \end{aligned}$$

$$\begin{aligned} 7) \quad \epsilon_{\Delta n_{2 \text{ phase}}} &= \sqrt{(0.61)^2 + 6(0.20)^2} \\ &= 0.83 \text{ mmoles.} \end{aligned}$$

In the one phase region, the error in Δn for the removal of one aliquot of gas is, from eq. 4,

$$10) \quad \epsilon_{\Delta n_1 \text{ phase}} = \frac{1}{1.21(783)} \sqrt{(150 \times 4.75)^2 \left[\left(\frac{4}{150} \right)^2 + \left(\frac{0.14}{4.75} \right)^2 \right] + (150 \times 0.231)^2 \left[\left(\frac{10}{150} \right)^2 + \left(\frac{0.15}{2.31} \right)^2 \right] + (150 + 6.44)^2 \left[\left(\frac{10}{150} \right)^2 + \left(\frac{0.15}{6.44} \right)^2 \right]}$$

$$= \frac{67.6}{947}$$

$$= 0.07 \text{ mmoles.}$$

The total error in the one phase region is

$$11) \quad \epsilon_{\Delta n_1 \text{ phase-total}} = \sqrt{9 \epsilon_{\Delta n}^2}$$

$$= \sqrt{9(0.07)^2}$$

$$= 0.21 \text{ mmoles.}$$

Referring back to eq. 6,

$$6) \quad \epsilon_{\Delta n_T} = \sqrt{\epsilon_{\Delta n_2 \text{ phase}}^2 + \epsilon_{\Delta n_1 \text{ phase}}^2}$$

$$= \sqrt{(0.83)^2 + (0.21)^2}$$

$$= 0.85 \text{ mmoles.}$$

As can be seen from eq. 2 the error in the composition is a function of that composition. As the error in the composition at the end of the 2 phase region was needed to calculate the error in the thermodynamic functions, the error at that point was calculated.

$$2) \quad \epsilon_x = 2 \left(\frac{1}{\Delta n_T} \right)^2 \sqrt{(\Delta n_T)^2 \epsilon_{\Delta' n}^2 + (\Delta' n)^2 \epsilon_{\Delta n_T}^2}$$

$\Delta' n$, in this case, is the hydrogen evolved from the 1 phase region.

$$\begin{aligned}
 \epsilon_x &= 2\left(\frac{1}{150.3}\right)^2 \sqrt{(150.3)^2(0.15)^2 + (2.7)^2(0.85)^2} \\
 &= 8.84 \times 10^{-5} (22.7) \\
 &= 0.002
 \end{aligned}$$

Thus the composition at the end of the 2 phase region at 510° is 0.036 ± 0.002 . Assuming that the 440, 470, and 560° isotherms can also be represented by the same average isotherm, then the percentage error in the composition value at the end of the 2 phase region is the same as for the 510° isotherm. This is so because eq. 2 can be shown to be equal to

$$\epsilon_x = x \sqrt{\left(\frac{\epsilon_{\Delta'n}}{\Delta'n}\right)^2 + \left(\frac{\epsilon_{\Delta n_T}}{\Delta n_T}\right)^2}$$

or

$$\frac{\epsilon_x}{x} = \text{percentage error in } x = \sqrt{\left(\frac{\epsilon_{\Delta'n}}{\Delta'n}\right)^2 + \left(\frac{\epsilon_{\Delta n_T}}{\Delta n_T}\right)^2}$$

As $\Delta'n$, Δn_T , $\epsilon_{\Delta'n}$, and $\epsilon_{\Delta n_T}$ are the same as in the 510° isotherm, $\epsilon_{x/x}$ is the same in all isotherms. Although the average isotherm does not represent the actual isotherms exactly, the number of aliquots removed from the reactor, and the attendant pressure changes, were fairly similar. Thus the error in using this assumption is very small.

Referring to Table 4, it can be seen that the experimental compositions for the end of the 2 phase regions at 510° exhibit a larger error than the calculated one. However, it is likely that there are other errors which have not been evaluated. Therefore the error ascribed to these values will be taken as ± 0.01 in the composition.

At pressures higher than the decomposition pressure, the following error is calculated assuming 5 removals of hydrogen with attendant 500 p.s.i. pressure changes.

$$\epsilon_{\Delta n_{\text{Total}}} = \sqrt{5 \epsilon_{\Delta n/\text{removal}}^2}$$

From eq. 4 the error in each removal is

$$\begin{aligned} \epsilon_{\Delta n/\text{removal}} &= \frac{1}{1.21(783)} \sqrt{(500 \times 4.75)^2 \left[\left(\frac{4}{500} \right)^2 + \left(\frac{0.14}{4.75} \right)^2 \right] + (500 \times 2.31)^2 \left[\left(\frac{10}{500} \right)^2 + \left(\frac{0.15}{2.31} \right)^2 \right] + (500 \times 6.44)^2 \left[\left(\frac{10}{500} \right)^2 + \left(\frac{0.15}{6.44} \right)^2 \right]} \\ &= \frac{142.5}{947} \\ &= 0.15 \text{ mmoles} \end{aligned}$$

$$\begin{aligned} \epsilon_{\Delta n} &= \sqrt{5(0.15)^2} \\ &= 0.34 \end{aligned}$$

The calculated number of mmoles evolved from the solid to form $\text{MgH}_{1.99}$ is 0.75. Although this is larger than the calculated error, the data from the empty run had to be extrapolated to these higher pressures. These extrapolated corrections were larger than the values to be corrected so that the accuracy of these measurements would be small.

Thermodynamic

From the equation for ΔF°

$$12) \Delta F^\circ = -RT \ln K = +RT \ln a_{\text{Mg}} f_{\text{H}_2}$$

the error in this value, $\epsilon_{\Delta F}$, can be calculated as follows.

$$13) \left(\frac{\epsilon_{\Delta F}}{\Delta F} \right)^2 = \left(\frac{\epsilon_T}{T} \right)^2 + \left(\frac{\epsilon_{\ln K}}{\ln K} \right)^2$$

or

$$\epsilon_{\Delta F} = \Delta F \sqrt{\left(\frac{\epsilon_T}{T} \right)^2 + \left(\frac{\epsilon_{\ln K}}{\ln K} \right)^2}$$

$$K = \frac{1}{a_{Mg} f_{H_2}} = \frac{1}{\gamma_{Mg} N_{Mg} \gamma'_{H_2} P_{H_2}}$$

γ = activity coefficient.

As Raoult's law has been assumed for the magnesium rich phases, $\gamma = 1$. For the purpose of finding the error, γ' can also be considered to be 1 as the error in this is negligible compared to N_{Mg} and P_{H_2} .

$$\left(\frac{\epsilon_K}{K} \right)^2 = \sqrt{\left(\frac{\epsilon_N}{N} \right)^2 + \left(\frac{\epsilon_P}{P} \right)^2}$$

$$\epsilon_K = K \sqrt{\left(\frac{\epsilon_N}{N} \right)^2 + \left(\frac{\epsilon_P}{P} \right)^2}$$

$$\frac{\epsilon_K}{K} = \epsilon_{\ln K} = \sqrt{\left(\frac{\epsilon_N}{N} \right)^2 + \left(\frac{\epsilon_P}{P} \right)^2}$$

$$14) \epsilon_{\Delta F} = \Delta F \sqrt{\left(\frac{\epsilon_T}{T} \right)^2 + \left[\frac{\left(\frac{\epsilon_N}{N} \right)^2 + \left(\frac{\epsilon_P}{P} \right)^2}{(\ln K)^2} \right]}$$

An equation of $\ln N_{Mg}$ as a function of temperature was derived by the method of least squares. The few points only justified a first degree equation which was found to be

$$15) \ln N_{Mg} = -2.30 \times 10^{-4} T + 0.159.$$

The difference in the experimentally determined value of N_{Mg} and the value calculated from the above equation was used as the error in N_{Mg} . These values are shown in Table 6.

Table 6

Calculation of ΔF°

Temp. °C.	Pressure atm.	N_{Mg} Experimental	Calculated	Fugacity ^{18,19} Coefficient	$K = a_{Mg}^f H_2$ ΔF° Kcal/mole	$K = P_{H_2}$ $\Delta'F^\circ$ Kcal/mole	$\Delta'F^\circ - \Delta F^\circ$ Kcal
560	224.6	0.907	0.928	1.06	8.993	9.020	0.027
510	108.9	0.965	0.953	1.03	7.315	7.345	0.030
470	61.2	0.969	0.973	1.02	6.100	6.113	0.013
440	34.7	0.980	0.989	1.01	5.055	5.058	0.003

As previously noted, the error in the temperature measurement is $\pm 2^\circ$.

The deviation in the pressure measurement is two fold. The first is the ± 5 p.s.i. variation in the reactor pressure gauge. Also, as can be seen from the graphs of the various isotherms, the pressure over the two solid phase region seemed to fall slightly as hydrogen was removed. This decrease amounted to about 2% in each case which introduces an additional error of $\pm 1\%$ from the median decomposition pressure. The reason for this fall is not known but may simply be a rate effect. The error in the pressure is therefore

$$\epsilon_P = \sqrt{\epsilon_{\text{gauge reading}}^2 + \epsilon_{\text{Decomposition pressure}}^2}$$

The final expression for the error in ΔF is

$$16) \quad \epsilon_{\Delta F} = \Delta F \sqrt{\left(\frac{\epsilon_T}{T}\right)^2 + \frac{\left(\frac{\epsilon_N}{N}\right)^2 + \frac{(\epsilon_{\pm 5}^2 + \epsilon_{1\%}^2)}{P^2}}{(\ln K)^2}}$$

In Table 6 are listed ΔF° 's calculated from eq. 12, the error in this value found from eq. 16, ΔF° calculated by assuming $a_{\text{Mg}^f\text{H}_2} = P_{\text{H}_2}$, and the difference in the two ΔF° values. As can be seen the difference is less than the calculated experimental error. Thus, the equation

$$17) \quad \Delta F^\circ = + RT \ln P_{\text{H}_2}$$

was used to calculate the thermodynamic functions.

The error in the free energy calculated from eq. 17 was more difficult to find. Although, when the equation of $\log P$ as a function of temperature was derived, the errors in the coefficients were not found, the sum of the deviations

of the $\log P$'s was calculated. From this twice the standard deviation was computed as

$$\begin{aligned} 2\sigma &= 2\sqrt{\frac{(\Delta \log P)^2}{n(n-1)}} \\ &= 0.004 \end{aligned}$$

From the following it can be seen that this was actually a measure of the percentage error in the pressure.

$$y = f(P) = \log P$$

$$dy = d(\log P)$$

$$= \frac{dP}{2.303 P}$$

$$2.303 \Delta y = \frac{\Delta P}{P} = \pm 0.009$$

Therefore

$$\Delta F^\circ = 2.303 RT \log (P \pm 0.009 P) .$$

Thus, the error in the free energy is a function of the pressure and must be calculated for each temperature and pressure. At 560° , this has a value of ± 16 cal. However, the errors, listed in Table 6 calculated when ΔF° is expressed as,

$$\Delta F^\circ = RT \ln a_{Mg} f_{H_2}$$

is 47 cal. at 560° . Therefore, as this expression for the free energy is more exact, and because the errors involved in the calculation of these deviations are more complete, an error of ± 50 cal. has been assigned to ΔF° .

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As the equations of ΔH° , ΔC_p° , and ΔS° (see equations 13, 14, and 16 of the theory section) are not simple functions of the pressure, the errors were even more difficult to determine. In the case of ΔH° , by far the main contribution to the computed value comes from the constant, which is the same constant as appears in the ΔF° equation. In the free energy expression, there are two large terms of about equal magnitude, one of which is the constant, which should incorporate most of the error in ΔF° . If it is assumed that these errors are equal, then the statistical percentage error could be written

$$\frac{\epsilon_{\Delta F^\circ}}{\Delta F^\circ} = \sqrt{2 \epsilon^2} = 1.4 \epsilon$$

Thus the percentage error in ΔH° should be

$$\frac{\text{percentage error } \Delta F^\circ}{1.4}$$

As this calculated error does not involve a number of the terms, a total error equal to that in ΔF° , ± 50 cal., has been assumed for ΔH° .

In the ΔS° , and especially ΔG_p° , calculations, the largest terms are determined by the coefficients which have smaller contributions to the free energy. While the percentage error in these coefficients might be large, they would contribute little to the overall error in the free energy, while at the same time, possibly causing large errors in ΔS° and ΔC_p° .

In the case of ΔC_p° , a minimum error may be determined as follows. As shown in Table 7, $\Delta C_p^\circ = -1.9$ cal./deg./mole. However, a plot of $\log P$ vs $1/T$ fits the experimental points fairly well but seems to fall off at the lower temperatures

Table 7

Thermodynamic Summary

	Magnesium Hydride		Magnesium Deuteride	
	From eq. of form $\log P = A/T + B \log T + CT + DT^2 + E$ 450 25	From eq. of form $\log P = A/T + B$ 450 25	From eq. of form $\log P = A/T + B$ 450 25	From eq. of form $\log P = A/T + B$ 450 25
Temp.				
ΔF° calories	$5,484 \pm 50$	$5,413$	$5,693 \pm 100$	$-8,246 \pm 400$
ΔH° calories	$-18,155 \pm 50$	$-18,075$	$-18,029 \pm 100$	$-18,029 \pm 500$
ΔC_p° cal./deg./mole	7.59 ± 1.9	0	0	0
ΔS° e.u.	-31.94 ± 0.23	-32.5	-32.8 ± 1.0	-32.8 ± 0.5
C_p° cal./deg./mole	21.8 ± 1.9	$-$	$-$	12.7 ± 2.0
S° e.u.	18.17 ± 0.23	18.4	21.5 ± 0.5	9.6 ± 0.5

so that the slope, and thus ΔH° , becomes more negative. If the curvature does not change, and there is no reason to think it should down to room temperature, then ΔC_P° should have a positive value. Therefore, the errors in ΔC_P° and $C_P^\circ \text{ MgH}_2$ are at least 1.9 cal./deg./mole.

For ΔS° , an upper limit to the error may be set by use of the relationship

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}$$

$$\epsilon_{\Delta S^\circ} = \sqrt{\left(\frac{\epsilon_{\Delta H^\circ}}{T}\right)^2 + \left(\frac{\epsilon_{\Delta F^\circ}}{T}\right)^2}$$

$$\epsilon_{\Delta S^\circ} = 0.23$$

If the errors in ΔF° and ΔH° are realistic, the uncertainty to be attached to the value of ΔS° is 0.23 e.u. at temperatures above 25°C.

For the deuteride, the equation which relates $\log P$ to the temperature is actually valid only within the range of the experimental conditions. The thermodynamic values calculated at these temperatures should be fairly accurate. To help in judging the correctness of the computed values at both high and low temperatures, the hydride data were treated in the same manner. In this case, as well as the deuteride, a straight line fits the experimental points fairly well in a $\log P$ vs $1/T$ plot except at lower temperatures where the pressure appears to fall off. In Table 7, the values computed for the hydride using both the precise equation and the one similar to the deuteride are listed. The uncertainties in the deuterium values are probably of about the same order of magnitude as the differences in the hydride values computed in the two different manners.

As ΔH° is constant, ΔC_p° is equal to zero. This is quite obviously wrong at the high temperature, but may be no more in error than it is for the hydride at 25°. The same is true of the heat capacity of magnesium deuteride.

The different values for ΔS° of the hydride are in fairly good agreement and thus the error in the deuteride should be relatively small. The entropy of the deuteride should also be fairly good.

SUMMARY

Experimental

1) The expressions relating the decomposition pressures and temperatures for magnesium hydride and magnesium deuteride are as follows:

Hydride

$$\log P = -4.090 \times 10^3/T - 2.441 \log T + 4.524 \times 10^{-3} T - 2.277 \times 10^{-6} T^2 + 1.321 \times 10^3$$

Deuteride

$$\log P = -\frac{4.00 \times 10^3}{T} + 7.26.$$

This equation is accurate only from 300 - 600°C. The experimentally determined points are listed in Table 2 and a curve drawn from the points is shown in Figure 5, while the pressures corresponding to various temperatures calculated from the above equations are tabulated in Table 8.

2) Both the hydride and deuteride systems are predominantly two phase. At the hydrogen-rich end of the composition range there is no solid solution at compositions less than $\text{MgH}_{1.99}$. At the magnesium-rich end, solid solution is exhibited for a small composition range. For temperatures of 440, 470, 510 and 560° this region extends to $\text{MgH}_{0.02}$, $\text{MgH}_{0.03}$, $\text{MgH}_{0.04}$ and $\text{MgH}_{0.10}$ respectively

Table 8
Calculated Decomposition Pressures

Temperature °C	Magnesium Hydride		Magnesium Deuteride	
	<u>Atmospheres</u>	<u>Psi</u>	<u>Atmospheres</u>	<u>Psi</u>
25	4.0×10^{-7}	6×10^{-6}		
50	4.6×10^{-6}	7×10^{-5}		
100	2.2×10^{-4}	3×10^{-3}		
150	4.4×10^{-3}	7×10^{-2}		
200	4.7×10^{-2}	0.7		
250	0.32	5		
300	1.6	23	1.9	28
350	5.8	85	6.9	102
400	17.8	262	20.8	305
450	45.6	671	53.5	786
500	102.7	1510	121.9	1792
550	203.9	2997	251.2	3693
600	368.7	5420	477.5	7019

for the hydride, and $\text{MgH}_{0.05}$ for the deuteride at 510° . The uncertainty in these compositions is ± 0.01 . In all cases, the upper pressure limit of these one-phase regions is from 200 - 600 p.s.i. below the corresponding decomposition pressure and there appears to be very little, solid decomposition between these limits. The final isotherms are shown in Figure 9.

3) Pure magnesium hydride was not prepared nor was it possible to prepare a product of constant composition. The explanation for this difficulty is not known. Although material of greater than 90% purity was made, it could not be repeated at will. The Metal Hydrides material, although of fairly high hydride content, still contained unreacted magnesium.

Thermodynamic

From equations 12, 13, 14, and 16 of the theory section, and the equation developed to express the experimental values of $\log P$, the following thermodynamic functions for the formation of magnesium hydride and magnesium deuteride were derived.

Hydride

$$\Delta F^\circ = -11.170 T \log T + 55.886 T + 20.703 \times 10^{-3} T^2 - 10.420 \times 10^{-6} T^3 - 18.716 \times 10^3$$

$$\Delta H^\circ = 4.850 T - 20.703 \times 10^{-3} T^2 + 20.840 \times 10^{-6} T^3 - 18.716 \times 10^3$$

$$\Delta C_p^\circ = -41.406 \times 10^{-3} T + 62.520 \times 10^{-6} T^2 + 4.850$$

$$\Delta S^\circ = 11.170 \log T - 41.406 \times 10^{-3} T + 31,260 \times 10^{-6} T^2 - 51.036$$

Deuteride

$$\Delta F^\circ = 32.81 T - 18,029$$

$$\Delta H^\circ = -18,029$$

Figure 9
Final Isotherms

FINAL ISOTHERMS

FIGURE 9

Numerical values for these quantities at 25° and 450°C are given in Table 7.

The expressions for the heat capacities of magnesium, hydrogen⁹ and deuterium¹¹ are,

$$C_P^{\circ} \text{ Mg} = -0.78 \times 10^5 / T^2 + 1.50 \times 10^{-3} T + 6.14$$

$$C_P^{\circ} \text{ H}_2 = 0.12 \times 10^5 / T^2 + 0.78 \times 10^{-3} T + 6.52$$

$$C_P^{\circ} \text{ D}_2 = 0.21 \times 10^{-3} T + 4.68 \times 10^{-7} T^2 + 6.83$$

The corresponding entropy expressions from eq. 17 of the theory section, and values for $S_{298.16}$ taken from the N.B.S. circular No. 500,¹⁰ are as follows:

$$S_{\text{Mg}}^{\circ} = 0.39 \times 10^5 / T^2 + 2.303 (6.14) \log T + 1.50 \times 10^{-3} T - 28.11$$

$$S_{\text{H}_2}^{\circ} = -0.06 \times 10^5 / T^2 + 2.303 (6.52) \log T + 0.78 \times 10^{-3} T - 6.11$$

$$S_{\text{D}_2}^{\circ} = 2.303 (6.83) \log T + 0.21 \times 10^{-3} T + 2.34 \times 10^{-7} T^2 - 4.41$$

From the various expressions for ΔC_P° , ΔS° , C_P° and S° above, the following equations are found:

Hydride

$$C_P^{\circ} = -0.66 \times 10^5 / T^2 - 39.13 \times 10^3 T + 62.50 \times 10^{-6} T^2 + 17.51$$

$$S^{\circ} = 0.33 \times 10^5 / T^2 + 40.33 \log T - 39.13 \times 10^{-3} T + 31.26 \times 10^{-6} T^2 - 85.26$$

Deuteride

$$S^{\circ} = 0.39 \times 10^5 / T^2 + 29.87 \log T + 1.71 \times 10^{-3} T + 2.34 \times 10^{-7} T^2 - 65.32$$

Values for the heat capacity and entropies at 25° and 450° are listed in Table 7.

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