5-1930

A study of the dissociation of calcium hydride

Kenneth Elwin Walker
Union College - Schenectady, NY

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A STUDY OF THE DISSOCIATION OF CALCIUM HYDRIDE

May 27, 1930   Kenneth Walker

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A thesis, presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry by

Kenneth Walker

Approved by *Charles B Hurd*

May 27, 1930

A STUDY OF THE DISSOCIATION OF CALCIUM HYDRIDE

INTRODUCTION

The calcium hydride equilibrium has been
investigated by a number of men but the results
obtained have been almost as diversified as the
number of workers. There is considerable doubt
as to the mechanism of the dissociation and the
compounds formed. Some workers claim evidence
of two hydrides while others found only the normal
hydride, CaH_2. In most of the previous work the
equilibrium has been more or less disturbed by the
volatility of the calcium and the hydride and also
the reaction of the calcium or the hydride on the
quartz containers. In this work an attempt has
been made to overcome these difficulties by en-
closing the solids in an iron or nickel cylinder
which is permeable to hydrogen gas at the temper-
atures of the dissociation. This should give more
accurate hydrogen pressures which is a measure of
the progress of the reaction since it is the only
gaseous component. This method can also be applied
to the measurement of dissociation of the hydrides
of barium and strontium.

HISTORICAL

In 1899 Moissan[1] found if calcium were heated to red in a stream of hydrogen a white crystalline compound of the formula CaH_2 was formed.

Later Gautier[2] found the CaH began to dissociate at about $700°C$. the dissociation increasing with increasing temperature.

In 1905 Guntz and Bassett[3] determined calorimetrically the heat of formation of the hydride to be -46,200 cals. Such a large exothermic heat of formation usually denotes a stable compound.

Moldenauer and Roll-Hansen[4] determined the equilibrium pressures and found two sets of values which gave values of $\Delta H = 20,600$ and 21,000 cals. for the heat of dissociation. They explained this by saying that the hydride dissociated in two steps forming a lower hydride CaH and that the sum of the heats of dissociation given above which was 41,600 cals. was the heat of dissociation from CaH_2 to Ca and H_2 which agreed fairly well with the calorimetric value.

Bronsted[5] also studied the equilibrium and obtained only one set of equilibrium pressures corresponding to the reaction

$$CaH_2 \longrightarrow Ca + H_2$$
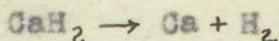
which gave him a graphical value of $\Delta H = 43,930$ cals. Bronsted

measured the heat of formation calorimetrically by
dissolving Ca and CaH_2 in hydrochloric acid and found
$\Delta H_{298°} = 45,100$ cals. He found no indication of the for-
mation of a lower hydride.

Later Kraus and Hurd[6] measured the equilibrium
and found values slightly lower than Bronsteds values
but while Bronsteds values only went to 750° C. Hurd and
Kraus measured the equilibrium up to 1000° C. They also
found no evidence of a lower hydride from the pressure
measurements. From their results they obtained graphi-
cally $\Delta H = 48,400$ cals.

Later Hurd and Small[7] and Hurd and Smith[8] made some
measurements with the Calcium and the calcium hydride
contained in an iron cylinder which was permeable to
hydrogen at the temperatures of the dissociation. They
expected to pervent the calcium or the hydride from
distilling out in the cooler portion of the reaction
tube and reduce the equilibrium pressures of the hydro-
gen. Their results show that with the closed iron cylin-
ders instead of obtaining higher hydrogen pressures
than with the open tubes they obtained lower equilibrium
pressures.

While the present was being carried on an article
by Gennete[9] was published in which the same method of
using iron cylinders was described. He however obtained

pressures of hydrogen slightly higher than other inves-
tigators by the earlier methods as was expected by Hurd,
Small and Smith. His results however do not follow a good
curve at the higher temperatures as shown in Curve 1.

At the same time Kasmir and Stemple[10] published
thier results in which, using the open iron tubes, they
obtained equilibrium pressures much higher than those of
previous investigators and believed they corresponded to
the equilibrium

$$2CaH_2 \rightarrow 2CaH + H_2$$
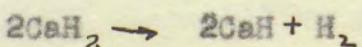
APPARATUS

The apparatus used in the determinations is shown
in plate 1 and 2. The calcium was freshly cleaned and the
surface free d from oxide and then inserted in an iron or
nickel cylinder and a tight fitting plug inserted in the
open end of the cylinder to prevent any escape of calcium
or hydride vapor from the cylinder. The cylinders were made
of the pure metals and the surfaces freed from oxide
coating. They were about $\frac{3}{8}$" outside diameter and walls
.05" thick. The lengths varied from about 3 $\frac{1}{2}$" to 4$\frac{1}{2}$".
The plugs to close the end were made from the same metals
and turned down so that they had to be driven in with a
hammer to insure a tight fit.

After the cylinders were located with about one gram

of the calcium metal they were placed in a clear quartz
tube which was connected with the glass system by a Kho-
tinsky cement joint. The whole system was ~~placed~~ evac-
uated and tested one or two days for leaks. The cylinder
was then heated to about 700°C. by an electric furnace
at which temperature the metal was permeable to hydrogen.
The calcium was then allowed to absorb about 70 cms. Pres-
sure of hydrogen and the system again evacuated. This
formed the hydride and the temperature was then raised a
little above 700°C. where dissociation of the hydride
began as shown by the manometer.

The temperature of the furnace was maintained con-
stant within one or two degrees by means of the arrange-
ment also shown in plate 1. Three ballast tubes of the
type U.V. 876 were connected in a series-parallel
arrangement so as to deliver a steady current to the
furnace with a voltage drop between 40 and 60 volts on
the tubes. The temperature was changed by a shunt
resistance. This gave very good temperature control.
The temperatures were measured by an alumel-chromel
thermocouple which was calibrated at the silver point.

The pressure measurements were made with a mercury
manometer and a very good cathetometer capable of
measuring pressures to within ± .01 cm. An attempt was
made to obtain measurements for the equilibrium when
approached from both sides by alternately increasing

and lowering the temperatures for successive readings.
Extreme care had to be taken that none of the calcium
was able to get out of the cylinders for if it did it
attacked the quartz liberating silicon and disturbing
the equilibrium considerably.

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RESULTS

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The first determinations were made with an iron
cylinder. In the previous work the iron and nickel
cylinders were used to hold the calcium but they were
open at one end. A small amount of calcium and the
hydride thus distilled into the cooler portions of
the quartz tube and while the equilibrium could be
reached in ten or fifteen minutes the hydrogen pressure
should be lower than the true equilibrium pressure due
to the condensation on the cooler portions of the tube.
Thus when closed cylinders were used higher hydrogen pressures
should be obtained than when open cylinders were used.
The results obtained with an iron cylinder agree fairly
well with those obtained by Hurd and Small[7] all the results
being lower than the results formerly obtained instead
of higher as predicted.

The equilibrium results obtained with the closed
iron cylinders are as follows:
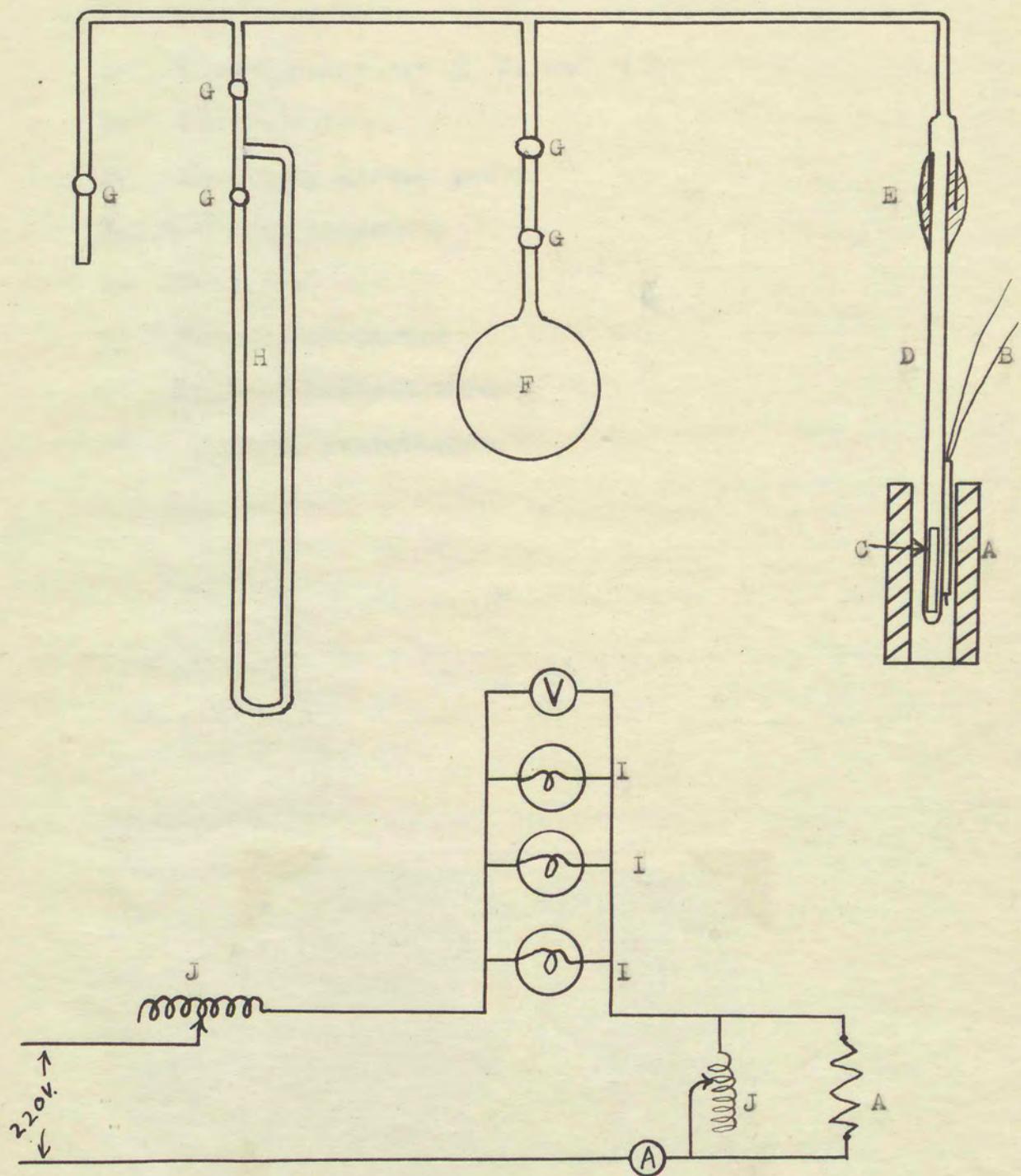
PLATE 1

(See next page)

KEY TO PLATE 1.

A-   Electric furnace

B-   Thermocouple

C-   Closed cylinders of Ca and CaH

D-   Quartz tube

E-   Khotinsky cement joint

F-   Hydrogen generator

G-   Stopcocks

H-   Mercury manometer

I-   Voltage ballast tubes

J-   Control resistances

PLATE   2
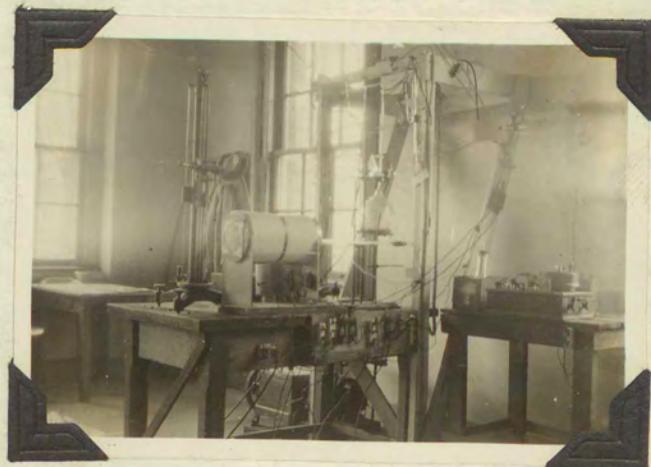
Temp.° K	$\frac{1}{T}°$K x10^6	Press. H$_2$ (cms.Hg.)	Log P
1089	919	2.15	.332
1121	892	3.95	.597
1140	877	6.63	.882
1160	862	7.95	.905

Since nickel behaves like iron towards hydrogen
at high temperatures nickel cylinders were next used. They
also had the advantage of containing fewer impurities that
would form hydrides than the iron cylinders. With the
nickel cylinders the pressures came higher than those ob-
tained with open cylinders as had been predicted. The nickel
also passed the hydrogen faster and made it possible to
obtain an equilibrium in one day where nearly three were
required with the iron cylinders. It was however found
that above about 960° C. the calcium was driven into the
pores of the nickel and the nickel would pass the hydrogen
only to a very slight extent so that it was impossible to
obtain equilibrium pressures above this temperature.
The results of the determinations with the nickel cylinders
are as follows:

Temp.° K.	$\frac{1}{T}°$K.x10^6	Pressures H$_2$ (cms. Hg.)	Log P
	Run. 1		
1090	917	3.93	.595
1126	887	7.75	.890
1155	866	13.65	1.135

Temp.° K	$\frac{1}{T}$ K°	Press, H_2 (cms. Hg)	Log P
1177	850	20.25	1.306
1210	827	37.22	1.571
Run 2.			
1044	959	1.33	.124
1065	941	2.04	.309
991	1009	.42	-.377
1088	919	3.26	.513
1109	903	5.21	.716
1131	884	8.01	.903
1082	924	2.84	.454

These results are plotted in Curve 1. and compared
with some of the results of other earlier investigators.
From the Clausius- Clapeyron equation

$$\frac{dp}{dt} = \frac{\Delta S}{\Delta V}$$

where ΔS and ΔV are the entropy and volume change re-
spectively
                when a vapor phase is being formed from a liquid
or solid phase. $\Delta V = V(gas) - V(liquid)$ and since for most
solids V(liquid) is negligible compared with V(gas), ΔV
equals V(gas) and if the gas obeys the perfect gas law
$\Delta V = \frac{RT}{P}$. Also from thermodynamics $\Delta S = \frac{\Delta H}{T}$. When these
substitutions are made the following is obtained

$$\frac{dp}{dt} = p \frac{\Delta H}{RT^2}$$

or

$$\frac{dp}{p} = \frac{\Delta H}{RT^2} \; dT$$

which upon integration gives

$$\ln p = \frac{-\Delta H}{RT} + constant$$

In this case the equilibrium studied can be considered
as measured by the pressure of the only component which
is a gas, that is the hydrogen and if the ordinary
expression for the equilibrium constant be set up the
$P_{H_2} = K_P$ the equilibrium constant if the log K_P is
plotted against $\frac{1}{T}$° K for the limited range of temperatures
involved here a straight line relationship should be
obtained. The slope of the curve will give ΔH which
is the heat of dissociation of the hydride into its
elements. In this case the reaction is endothermic

KEY TO CURVE 1.

Curves from data of previous investigators.

    1. Using open iron cylinders.

        ⊙ Kraus and Hurd

    2. Using closed iron cylinders.

        ⊡ Hurd and Small

        △ Hurd and Smith

        ⊙ Cennete

Curves from data of this experiment.

    1. Using closed iron cylinders

        ✗ From data on top of page 9.

    2. Using closed nickel cylinders.

        ◎ Data from Run 1. page 9.

        ▣ Data from Run 2. page 9.

Curve I.

GENERAL ELECTRIC COMPANY, SCHENECTADY, N. Y., U.S.A.
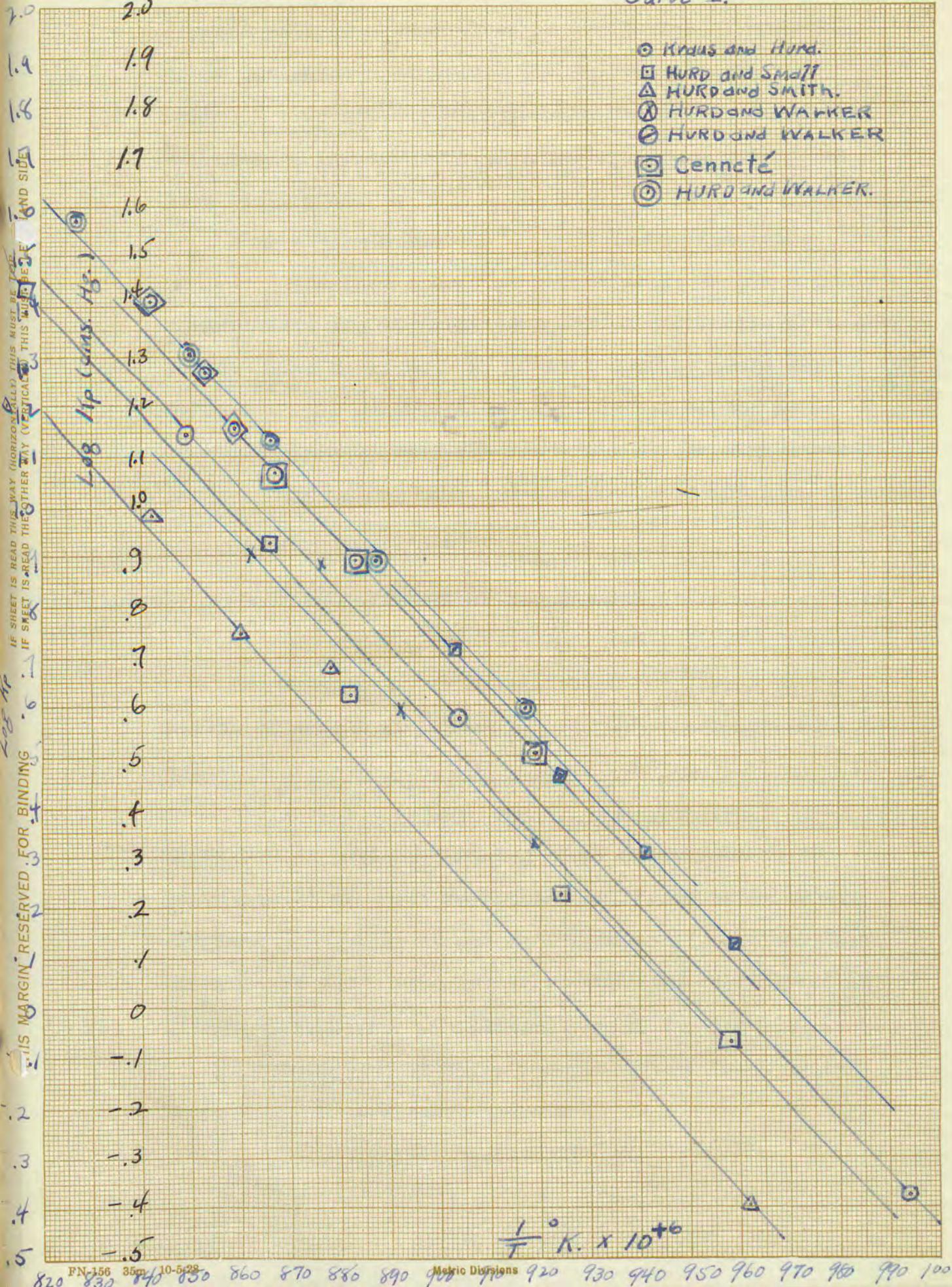
and the heat of dissociation is quite high so according to Le Chatelier's principle the dissociation should begin at a relatively high temperature and increase with increase in temperature. All investigators have found this to be true.

From the relation $\Delta F^0 = -RT \ln K_P$ the values of ΔF^0 the free energy of dissociation at the different temperatures can be calculated from the hydrogen pressures found. This notation ΔF^0 is that used by Lewis and Randall[11] to designate the free energy change in a reaction starting with the reactants at one atmosphere pressure and ending with the resultants at the same pressure.

DISCUSSION OF THE RESULTS

The free energy of dissociation of calcium hydride can be expressed as a function of the temperature by the relation -

$$\Delta F^0 = \Delta H^0 - \Sigma\alpha T\ln T - \frac{\Sigma\beta}{2} T^2 - \frac{\Sigma\gamma}{6} T^3 + IT$$

where $\Sigma\alpha, \Sigma\beta$ and $\Sigma\gamma$ are the usual summations of the constants of the heat capacities of the products minus the heat capacities of the reactants and I is a constant. If ΔH_0 is taken from the value obtained calorimetrically by Bronsted as $\Delta H_0 = 44,800$ cal's. and the average ΔC_P of the reaction taken as 1.0 as calculated by Lewis and Randall[11] the equation becomes -

$$\Delta F^0 = 44,800 - 1.0\ T\ln T + IT$$

The calorimetric value of ΔH is taken instead of the experimental value because this is found to give a more constant value of I. From the experimental data obtained it is possible to calculate ΔF^{o} at several temperatures from the relation $\Delta F^{o} = - RT\ln K_{p}$ and by substituting these in the ΔF^{o} equation above values of I can be obtained. The constancy of these values of I obtained will determine to some extent the reliability of the data. Some of the values of I obtained are tabulated below giving the experimental value of ΔF^{o} used to obtain I.

ΔF^{o}	I	Temp. ^{o}K
-2945 cals.	-36.65	1090
-4570	-3670	1126
-5980	-36.85	1155

Thus an equation for the variation of ΔF^{o} with the temperature has been obtained. From it $\Delta F^{o}_{298^{o}}$ was calculated and found to be 32,165 cal's. Using the calorimetric value of $\Delta H_{298^{o}} = 45,100$, $\Delta S^{o}_{298^{o}}$ can be calculated for the dissociation by substitution in the formula

$$\Delta S^{o}_{298^{o}} \quad \frac{\Delta F^{o} - \Delta H^{o}}{298^{o}}$$

Lewis and Randall[11] calculate $\Delta S^{o}_{298^{o}}$ from Bronsted's data to be 34.6 cal's. They then calculate $\Delta S_{298^{o}}$ from the postulates of the third law of thermodynamics and obtain the value $\Delta S_{298} = 30.58$ cals. They consider Bronsted's determinations to be in error because they do

not agree more nearly with the ΔS^o obtained from the
third law considerations but the specific heat data which
they used to obtain this value is not known very accurately
so it is not surprising that there should be a deviation.
From the results using the closed cylinders the values of
ΔF^o should be higher than those of Bronsted and thus give
a higher entropy of dissociation. This of course would
deviate more from the value calculated by the third law.
The value of $\Delta S^o_{298^o}$ found by this experiment is 43.4 cals.
                                                                gr.mol.
which is considerably higher than the theoretical value.
When the exact mechanism of the reaction is known and when
the specific heat data is obtained more accurately the
values of ΔS^o will probably be found to agree more closely
than those calculated previously.

From considerations of the curves plotted it will be
seen that the determinations with closed iron cylinders
made in this laboratory are lower than those with open
cylinders when according to theoretical considerations
they should be higher since with the closed cylinders the
calcium is unable to distill out and lower the vapor
pressure. There has been no explanation found here unless
it is due to some specific action of the iron on the
reaction. Cennete's [9] results are more in accord with
theoretical considerations and are in fair agreement with
the ones obtained using nickel cylinders. However, from
the curve it will be seen that his results deviate from
the straight line relationship at the higher temperatures

which deviation is not exhibited by the nickel cylinders.
Since the curves for the various determinations did not
coincide it was thought that perhaps large amounts of
hydrogen were absorbed by the nickel and given out at
the higher temperatures. This was tested by using an
empty nickel cylinger. It was found that some hydrogen
was absorbed but that scarcely any was given out as the
temperature was raised above 900^{0} C. Another explanation
of this variation in hydrogen pressure found when different
samples of calcium were used was given by Ephriam and
Michel[12]. They found evidences of a solid solution
formed by calcium and calcium hydride and this of course
would effect the hydrogen pressure when different relative
amounts of the two were used. Kraus and Hurd[6] however, tested
this out and found no evidence of solid solutions. It
seems that if a solid solution were formed that the curve
Log K_p against $\frac{1}{T}$ would not obey the straight line relation-
ship at all. A more logical explanation seems to be that
the iron and the nickel have some specific effect on the
reaction.

A number of investigators have obtained a second set
of dissociation pressures which they assign to a lower
hydride of formula CaH . From the two curves it was
found that the heat of dissociation was about equally
divided between the two reactions:

$$2\ Ca + H_2 \longrightarrow 2\ CaH$$
$$2\ CaH + H_2 \longrightarrow 2\ CaH_2$$
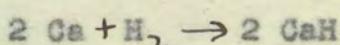
The normal hydride CaH_2 was found to be white
crystalline powder in appearance while the subhydride
was a dark gray powder. Kammir and Stempel[10] found

values of hydrogen pressures much higher than those
obtained by other workers and found $\Delta H = 22,600$
approximately. They thought this was the reaction
forming the normal hydride from the subhydride but
they found little evidence of a dissociation pressure
of the subhydride. Later C. W. Johnson working in the
laboratory with Kraus and Hurd prepared the subhydride
and found it to be scarcely volatile at the temperatures
of 800 - 1000 $^{\circ}$ C. The heat of fusion of calcium which
melts at 810 $^{\circ}$ C. is about $2000 \frac{\text{cals.}}{\text{gr.mol}}$ and the dissociation
curve should show a change in slope at this point but
none is found even when the closed cylinders are used in
this experiment. Another fact found in the open cylinder
measurements seems to substantiate the non-existence of
metallic calcium. At the temperatures at which the
dissociation was determined by Kraus and Hurd the vapor
pressure of the calcium was high enough so that all the
calcium should have distilled out of the cylinder in
short time but only a very small amount distilled out.
Apparently all this can be explained by the formation of
a lower hydride which is almost involatile and thus we
would get no inflection of the dissociation curve at
810 C. as the melting point of the pure calcium. The lower
hydride is apparently formed at lower temperatures and when
the dissociation is measured it is according to the equation-

$$2CaH_2 \longrightarrow 2CaH + H_2$$
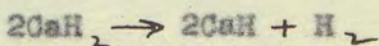
The curves plotted using the closed cylinders nearly all have the same slope which indicated the same value of ΔH for the reaction but they differ by a constant. This may be due to the fact that the mechanism of the reaction does not take place as has been explained by the formation of a lower hydride or the different cylinders used in each set of measurements may have a slightly different specific effect on the reaction. In any case the value of ΔH obtained from the curves is $\Delta H_{1073°} = 48700$ cals. which is gives a value of $\Delta H_{298°} = 47,900$ as compared with $\Delta H_{298} = 45,100$ cals. obtained calorimetrically by Bronsted.

From an examination of the iron and nickel cylinders after they had been used a grayish white powder was found along with what appeared to be pure calcium. If an X-ray examination were made of the substances found in the cylinder it might be possible to find evidence of the presence of pure calcium or the subhydride and to prove or disprove this theory of the mechanism of the reaction. The powder was a grayish white. Thus it might be partly white CaH_2 and gray CaH or what appeared to be metallic calcium might have been the CaH. Above 960° C.one of the substances in the nickel cylinders was driven into the pores of the cylinder thus destroying its permeability to the hydrogen and rendering further determinations

with that cylinder. This method could be applied to measurements of the dissociation of the hydrides of barium and strontium also. It was originally intended to make some determinations in connection with this paper but there was not sufficient time left. From some of the data already known the results can be predicted in a qualitative way. The heats of dissociation of barium hydride and strontium hydride have been found to be respectively $\Delta H = 40,900$ cals. and 42,200. From these values it can be predicted that calcium hydride is more stable than strontium hydride which in turn is more stable than barium hydride. Also the barium hydride will begin to dissociate at temperatures lower than either of the other two and also strontium hydride begins to dissociate at lower temperatures than calcium hydride does and the dissociation of all three increases with an increase in temperature.

CONCLUSIONS

A new and more accurate method for measuring the dissociation pressures of hydrogen from calcium hydride has been developed. A value of the entropy of dissociation of calcium hydride has been found to be $\Delta S^{\circ}_{298} = 43.4$ cals. which is not in agreement with the value obtained by the third law of thermodynamics. A value of $\Delta H_{298^{\circ}} = 47,900$ cals. for the heat of dissociation was found from the experimental curve. Further evidence for the existence of a sub

of a sub hydride of calcium has been found but no
evidence of any series of dissociation pressures
corresponding to the formation of a lower hydride as

$$2Ca + H_2 \longrightarrow 2CaH$$
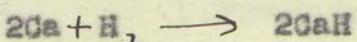
was found showing that if CaH was present it was
stable at the temperatures at which the normal hydride
dissociated into the subhydride. It was shown that
the results obtained by using iron cylinders do not
agree with those expected on theoretical grounds
while the results obtained with nickel cylinders do.
From the fact that the curves plotted do not all
coincide but are displaced from each other it was
suggested that the iron and nickel may have some
specific action on the process. It is possible by
applying the same methods to measure the dissociation
pressures of barium hydride and strontium hydride

and a qualitative prediction of the results which
would be obtained was made.

BIBLIOGRAPHY

(1) Moissan   Compt. rend.   127,- 29 (1899)

(2) Gautier   Compt. rend.   134, 1108 (1902)

(3) Guntz   Ann.Chim.   20, 5-33 (1923)

(4) Moldenauer and Roll-Hansen

              Zts. anorg. Chem. 82, 130-4 (1913)

(5) Bronsted   Zts. Electro. Chem. 20,81-83 (1914)

(6) Kraus and Hurd   J.A.C.S. 45, 2559   (1923)

(7) Hurd and Small   Thesis , Union College (1927)

(8) Hurd and Smith   Thesis , Union College (1928)

(9) Gennete   Compt. rend.   189, 579-81 (1929)

(10)Kasmir and Stemple

            Zts. anorg. allgem. Chem. 181, 83 (1929)

(11)Lewis and Randall

              "Thermodynamics" Mc Graw-Hill Pub. Co.(1923)

(12)Ephriam and Michel

            Helvet. Chim. Acta 4, 907 (1921)