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A STUDY OF THE DISSOCIATION OF CALCIUM HYDRIDE

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A STUDY OF THE DISSOCIATION OF CALCIUM HYDRIDE

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

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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 enclosing the solids in an iron or nickel cylinder which is permeable to hydrogen gas at the temperatures 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

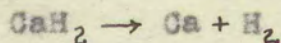
In 1899 Moissan¹ found if calcium were heated to red in a stream of hydrogen a white crystalline compound of the formula CaH_2 was formed.

Later Gautier² found the CaH began to dissociate at about 700°C . the dissociation increasing with increasing temperature.

In 1905 Guntz and Bassett³ determined calorimetrically the heat of formation of the hydride to be $-46,200$ cal. Such a large exothermic heat of formation usually denotes a stable compound.

Moldenauer and Roll-Hansen⁴ determined the equilibrium pressures and found two sets of values which gave values of $\Delta H = 20,600$ and $21,000$ cal. 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 $41,600$ cal. was the heat of dissociation from CaH_2 to Ca and H_2 which agreed fairly well with the calorimetric value.

Bronsted⁵ also studied the equilibrium and obtained only one set of equilibrium pressures corresponding to the reaction



which gave him a graphical value of $\Delta H = 43,930$ cal. Bronsted

measured the heat of formation calorimetrically by dissolving Ca and CaH_2 in hydrochloric acid and found $\Delta H = 45,100$ cal. He found no indication of the formation of a lower hydride.

Later Kraus and Hurd⁶ measured the equilibrium and found values slightly lower than Bronsted's values but while Bronsted's 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 graphically $\Delta H = 48,400$ cal.

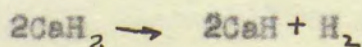
Later Hurd and Small⁷ and Hurd and Smith⁸ made some measurements with the Calcium and the calcium hydride contained in an iron cylinder which was permeable to hydrogen at the temperatures of the dissociation. They expected to prevent the calcium or the hydride from distilling out in the cooler portion of the reaction tube and reduce the equilibrium pressures of the hydrogen. Their results show that with the closed iron cylinders 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 Cennete⁹ was published in which the same method of using iron cylinders was described. He however obtained

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pressures of hydrogen slightly higher than other investigators 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 Stemple¹⁰ 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



APPARATUS

The apparatus used in the determinations is shown in platell and 2. The calcium was freshly cleaned and the surface free d fromoxide 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 tooclose 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 Khotinsky cement joint. The whole system was ~~placed~~ evacuated 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. Pressure 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 constant within one or two degrees by means of the arrangement 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 $\pm .01$ cm. An attempt was made to obtain measurements for the equilibrium when approached from both sides by alternately increasing

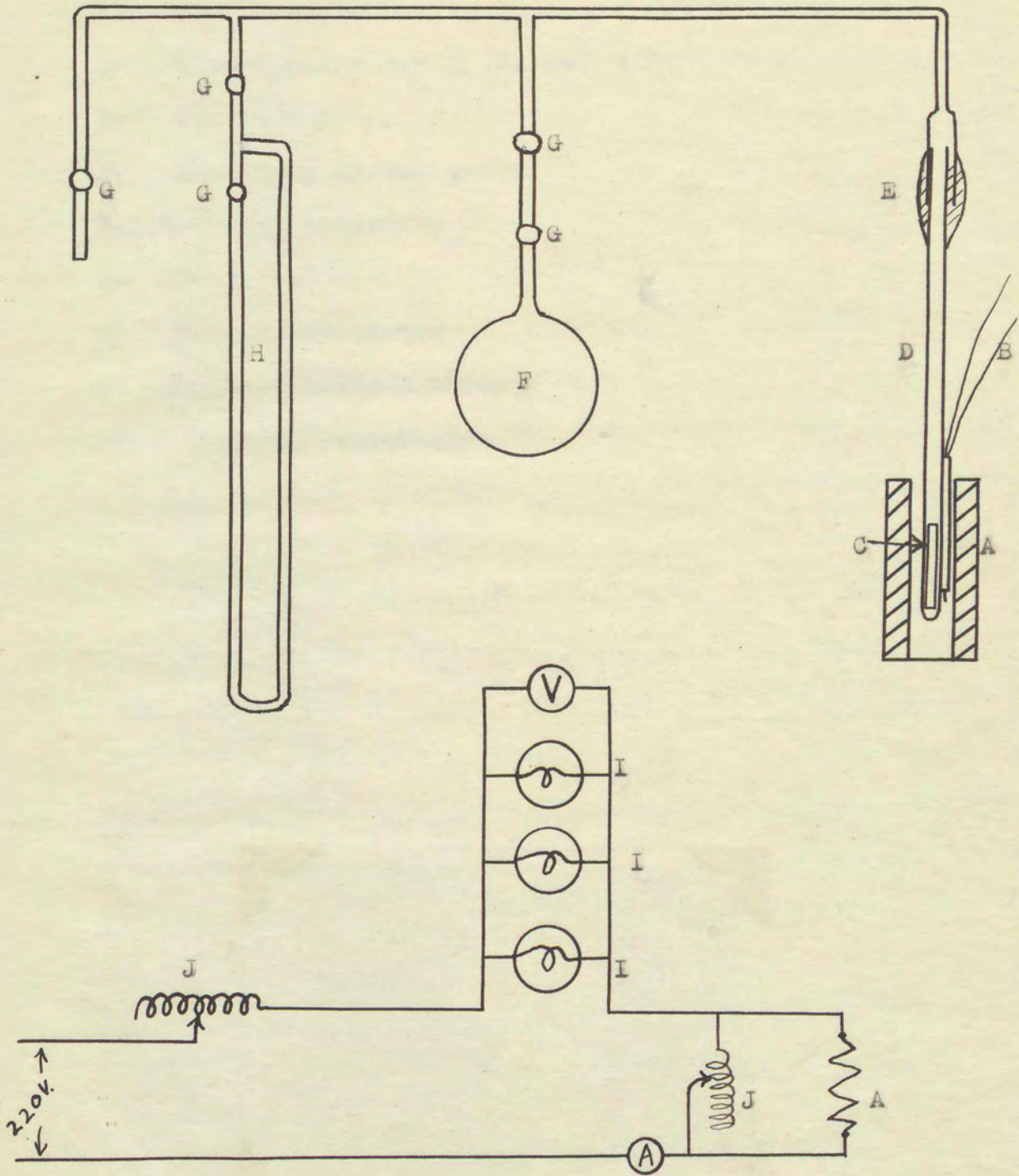
and lowering the temperatures for successive readings. Extreme care had to be taken that none of the calcium was able to get out of the cylinders for if it did it attacked the quartz liberating silicon and disturbing the equilibrium considerably.

RESULTS

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 Small⁷ 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	$\frac{1}{T} \text{ } ^\circ\text{K} \times 10^6$	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 obtained 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.	$\frac{1}{T} \text{ } ^\circ\text{K} \times 10^6$	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	(10) 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

(11)

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 respectively when a vapor phase is being formed from a liquid or solid phase. $\Delta V = V(\text{gas}) - V(\text{liquid})$ and since for most solids $V(\text{liquid})$ is negligible compared with $V(\text{gas})$, ΔV equals $V(\text{gas})$ 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

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

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

X From data on top of page 9.

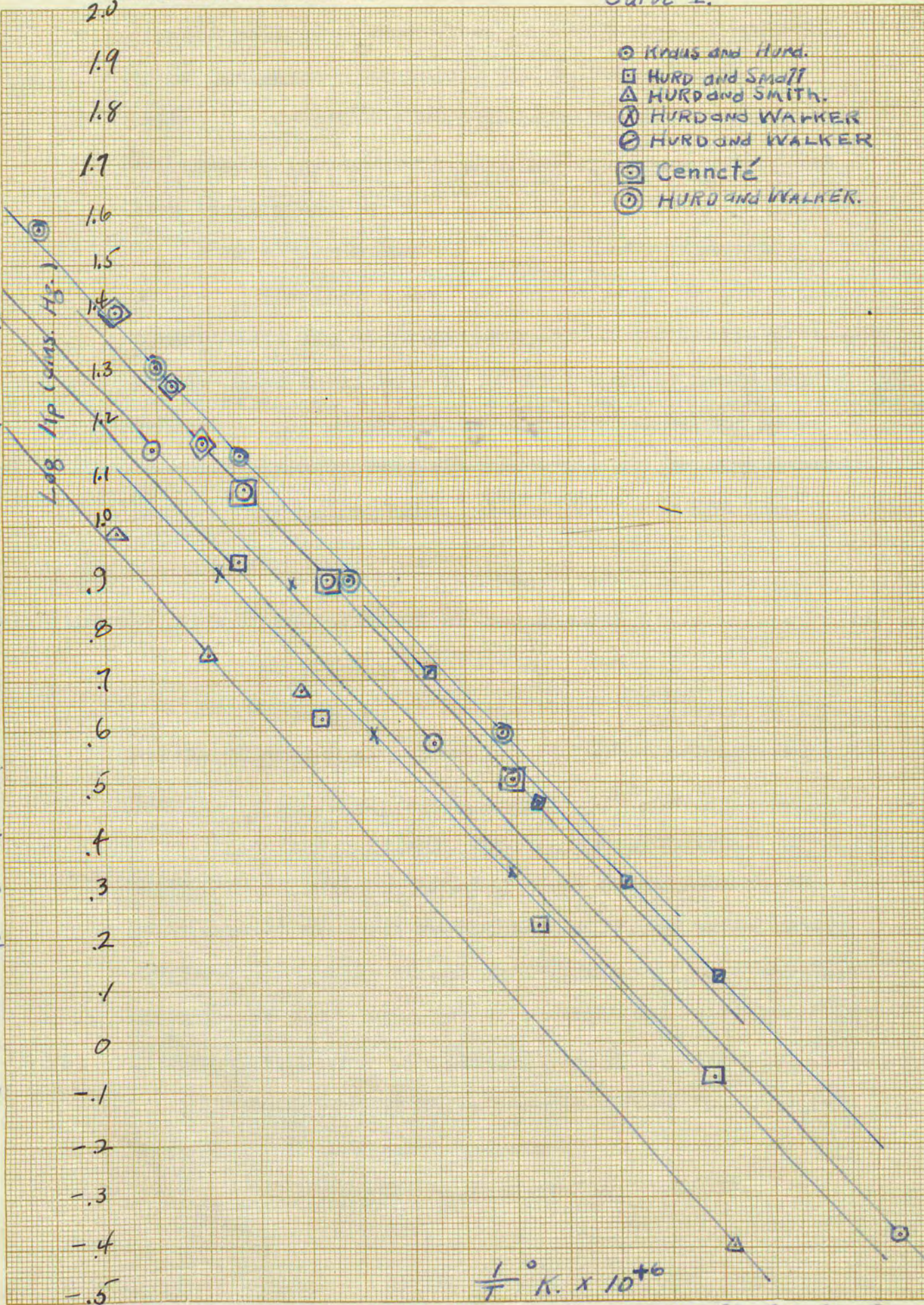
2. Using closed nickel cylinders.

⊙ Data from Run 1. page 9.

▣ Data from Run 2. page 9.

CURVE I.

IF SHEET IS READ THIS WAY (HORIZONTALLY) THIS MUST BE THE CASE. IF SHEET IS READ THE OTHER WAY (VERTICALLY) THIS MUST BE THE CASE. THIS MARGIN RESERVED FOR BINDING.



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 $\Delta F^\circ = -RT \ln K_p$ the values of ΔF° the free energy of dissociation at the different temperatures can be calculated from the hydrogen pressures found. This notation ΔF° 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 -

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

where $\sum \alpha$, $\sum \beta$ and $\sum \gamma$ 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° is taken from the value obtained calorimetrically by Bronsted as $\Delta H^\circ = 44,800$ cal's. and the average ΔC_p of the reaction taken as 1.0 as calculated by Lewis and Randall¹¹ the equation becomes -

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

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° at several temperatures from the relation $\Delta F^\circ = -RT \ln K_p$ and by substituting these in the ΔF° 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° used to obtain I .

ΔF°	I	Temp. ^o K
-2945 cal's.	-36.65	1090
-4570	-36.70	1126
-5980	-36.85	1155

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

$$\Delta S_{298}^\circ = \frac{\Delta F_{298}^\circ - \Delta H_{298}^\circ}{298}$$

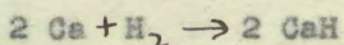
Lewis and Randall calculate ΔS_{298}° from Bronsted's data to be 34.6 cal's. They then calculate ΔS_{298}° from the postulates of the third law of thermodynamics and obtain the value $\Delta S_{298}^\circ = 30.58$ cal's. They consider Bronsted's determinations to be in error because they do

not agree more nearly with the ΔS° 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° 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 $\Delta S^\circ_{298^\circ}$ found by this experiment is $43.4 \frac{\text{cals.}}{\text{gr.mol.}}$ 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° 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. Gennete'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

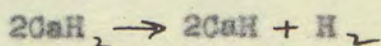
which deviation is not exhibited by the nickel cylinders. Since the curves for the various determinations did not coincide it was thought that perhaps large amounts of hydrogen were absorbed by the nickel and given out at the higher temperatures. This was tested by using an empty nickel cylinder. It was found that some hydrogen was absorbed but that scarcely any was given out as the temperature was raised above 900° C. Another explanation of this variation in hydrogen pressure found when different samples of calcium were used was given by Ephraim and Michel¹². 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 Hurd⁶ however, tested this out and found no evidence of solid solutions. It seems that if a solid solution were formed that the curve $\log H_p$ against $\frac{1}{T} \cdot K$ would not obey the straight line relationship 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:



The normal hydride CaH_2 was found to be white crystalline powder in appearance while the subhydride was a dark gray powder. Kammir and Stempel¹⁰ 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 $800 - 1000^{\circ} \text{C}$. The heat of fusion of calcium which melts at 810°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-



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 $\Delta H_{1073^\circ} = 48700$ cal. which gives a value of $\Delta H_{298^\circ} = 47,900$ as compared with $\Delta H_{298^\circ} = 45,100$ cal. obtained calorimetrically by Bronsted.

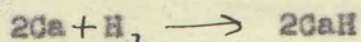
From an examination of the iron and nickel cylinders after they had been used a grayish white powder was found along with what appeared to be pure calcium. If an X-ray examination were made of the substances found in the cylinder it might be possible to find evidence of the presence of pure calcium or 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 $\Delta H = 40,900$ cal. 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 $\Delta S_{298}^{\circ} = 43.4$ cal. which is not in agreement with the value obtained by the third law of thermodynamics. A value of $\Delta H_{298}^{\circ} = 47,900$ cal. 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



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.

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