

under way, however, a series of experiments in which getters are dosed with pure gases such as hydrogen, water vapor, etc. These will be reported later also.

The curves obtained from getters in vacuum suggest that the final clean-up of traces of gas in vacuum tubes is due to voltage discharge, *i. e.*, voltage clean-up. We are undertaking some experiments of this effect both without getters and in their presence.

Summary

Measurements made on a series of chemically active getters show that differences in the previous treatment of the getters to remove gas are of far greater importance than differences between the getters themselves in production of high vacuum. Poorly degassed getters absorb residual gas slowly and reach equilibrium at higher pressures than those attained by more gas-free material. These pressures do not depend on temperatures between 0 and 90°.

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THE THERMAL DISSOCIATION OF CALCIUM HYDRIDE

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Introduction

The thermal dissociation of the hydrides of the alkali metals and of the alkaline earth metals has been the subject of considerable study. Various methods have been used, the general procedure being to heat the solid hydride to a definite temperature and measure the equilibrium pressure of the gaseous hydrogen.

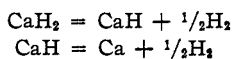
In the earlier studies little or no attempt was made to shield the glass or quartz system from possible chemical action with the metal hydrides or their dissociation products. This action is serious at the high temperature at which calcium hydride undergoes appreciable dissociation. Recent investigators have attempted to shield the quartz tubing from chemical action. In the present paper, the writers describe an apparatus which is the result of experiments over a period of about four years. The apparatus is the only one which has been found to work satisfactorily with calcium hydride. It will, we believe, give satisfactory results in any of the higher temperature hydride investigations. Results are given here for the dissociation of calcium hydride. The dissociation of barium hydride is being studied and it is hoped that work on strontium hydride may be started soon.

Historical

Calcium hydride is easily prepared by heating metallic calcium or certain alloys of calcium in hydrogen gas. The work of Guntz and Bassett,¹ of Moissan,² and of Brönsted,³ is typical. Recently, Proskurnin and Kasarnowsky⁴ have used the utmost care in preparing and handling the product. It is interesting to note, however, that the observations of the different investigators on the rate at which hydrogen is absorbed by the heated metallic calcium do not agree.

The results of the several studies on the thermal dissociation of calcium hydride appear to fall into two classes. The results of some investigators show a series of equilibrium pressures and temperatures which are reproducible and which fall upon a single curve. This curve is typical of a monovariant equilibrium consisting of a gas phase with one or more condensed phases. The results of Brönsted,³ of Kraus and Hurd,⁵ and of Remy-Cenneté,⁶ show only one equilibrium curve.

Other investigators have found evidence that more than one equilibrium is possible, depending upon the relative proportions of calcium and hydrogen present. Moldenhauer and Roll-Hausen⁷ believe that the dissociation takes place in two stages according to the equations



Kassner and Stempel⁸ have also found two equilibrium curves. The results of Ephraim and Michel,⁹ and those of Hüttig and Brodkorb,¹⁰ also show the apparent existence of more than one type of equilibrium, depending upon the relative amount of hydrogen which has been withdrawn from the original calcium hydride.

A source of error, common to the work which has been mentioned, is the possibility that calcium hydride or some solid product of the dissociation, may come into contact with the quartz container. Calcium hydride and quartz react at the elevated temperatures employed, setting free gaseous hydrogen. Hüttig and Brodkorb¹⁰ found a steady increase in the pressure of hydrogen when the system was held at constant temperature. On the other hand, Kassner and Stempel⁸ have shown by experiment that only a negligible loss of solid out of the equilibrium mixture occurred in their

¹ Guntz and Bassett, *Compt. rend.*, **140**, 863 (1905).

² Moissan, *Ann. chim. phys.*, **7**, 18, 289 (1899).

³ Brönsted, *Z. Elektrochem.*, **20**, 81 (1914).

⁴ Proskurnin and Kasarnowsky, *Z. anorg. allgem. Chem.*, **170**, 301 (1928).

⁵ Kraus and Hurd, *THIS JOURNAL*, **45**, 2559 (1923).

⁶ Remy-Cenneté, *Compt. rend.*, **189**, 579 (1929).

⁷ Moldenhauer and Roll-Hausen, *Z. anorg. Chem.*, **82**, 130 (1913).

⁸ Kassner and Stempel, *Z. anorg. allgem. Chem.*, **181**, 83 (1929).

⁹ Ephraim and Michel, *Helv. Chim. Acta*, **4**, 907 (1921).

¹⁰ Hüttig and Brodkorb, *Z. anorg. allgem. Chem.*, **153**, 309 (1926).

experiments. In the work of Kraus and Hurd,⁵ the calcium hydride was held in a vertical iron cylinder, with the lower end closed and the upper end open. The purpose of the iron cylinder was to protect the quartz tube. Some blackening of the quartz tube occurred, however, near the mouth of the iron cylinder.

Another possible source of error in these experiments is, obviously, that some of the solid products of decomposition may sublime to a cooler part of the quartz tube. Here they may reabsorb hydrogen, reducing the measured pressure and giving a false value for the equilibrium pressure at the temperature measured. The present study was made to eliminate these possible sources of error.

Apparatus

The logical improvement in the apparatus used for the determination of the dissociation pressure of calcium hydride would be to hold the calcium hydride inside the quartz tube in a closed container which would be permeable to hydrogen but not to calcium or calcium hydride. There are few such materials.

It was found that platinum or palladium could not be used, since small pieces of these metals alloyed with calcium. A long series of experiments was made, using closed cylinders of pure iron.¹¹

This material was abandoned during 1929 when we found that consistent results could not be obtained. We note that Remy-Cennet⁶ has recently used the same method with one difference. He used an iron cylinder with a thin sheet of iron welded over one end.

We have found that nickel is the best material which we have tried. It is possible that cobalt might work successfully. The results with nickel over a period of a year have been so successful that we are prepared to recommend nickel.

The apparatus used is shown in Fig. 1. A clear quartz tube, A, 16-mm. in diameter and 102 cm. long was supported horizontally, in the electric furnace D. A chromel-alumel thermocouple B was so placed that its end touched the quartz tube even with the nickel cylinder C.

The nickel cylinder C was made of a 10.2 cm. length of pure nickel tubing. The wall thickness was 1.27 mm. and the outside diameter 9.6 mm. Two short tapered plugs of pure nickel were turned in a lathe. The short cylindrical tube and the plugs were carefully cleaned. A plug was driven in one end of the short tube. Several pieces of freshly cleaned calcium were inserted in the cylinder and the other nickel plug inserted. These operations were carried out in a standard hydrogen bottle, the calcium having been cleaned in the bottle before being inserted in the cylinder. The calcium was a special pure calcium secured from the Research Laboratory of the General Electric Company. The plugs were pounded into the cylinder. Of six cylinders, made and filled in this way, two have leaked and four have been satisfactory at high temperatures.

¹¹ Unpublished thesis, Douglas Small, Union College, 1927; unpublished thesis, Dudley C. Smith, Union College, 1928.

The outside of the nickel cylinder was cleaned and the cylinder was pushed to the end of the quartz tube. A connection was made by means of a glass tube F to the glass measuring system. The tube F must be slid over the quartz tube A and the de Khotinsky joint E must be built up outside the glass tube F. If a glass tube should be inserted into the end of the quartz tube and a de Khotinsky joint built over the end of the quartz tube, it will always soften and suck in when the inner end of the quartz tube is at temperatures of 800° or over, since the clear quartz transmits radiation very well from its hot end to the cement at the cool end. An ordinary vacuum manometer G and a connection H to a vacuum pump complete the apparatus. The mercury manometer G was read by a high grade cathetometer, reading to 0.01 cm.

The chromel-alumel thermocouple B was calibrated at several points. The cold end was kept in a mixture of cracked ice and distilled water in a vacuum bottle.

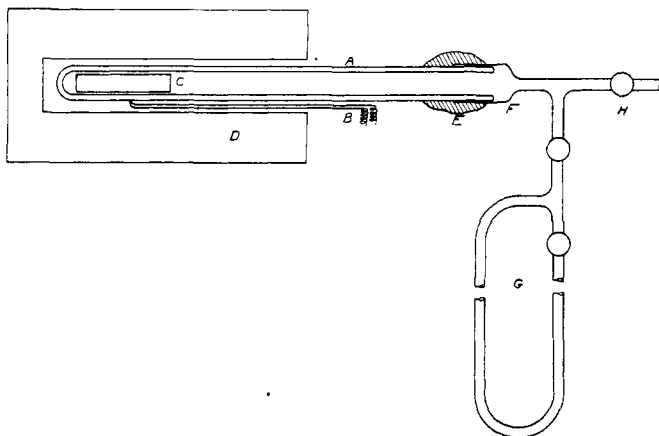


Fig. 1.—Apparatus employed in determining the dissociation pressures of calcium hydride.

Current through the electric furnace D was controlled, in spite of line voltage variations of as much as 10 volts by the use of UV-876 ballast tubes. One tube or two or three in parallel were used in series with the furnace on a 220 volt a. c. line. The single tube or the parallel two or three tube combinations gave constant currents of 1.7, 3.4 or 5.1 amps. A variable resistance shunted across the furnace allowed any fraction of the current to pass through the furnace. The necessary ammeters and voltmeters were included in the circuit.

A run was made as follows. A cylinder with a fresh charge of calcium, 1.0 to 1.4 g., was placed in tube A. The glass system was attached. The system was pumped out and the furnace raised to a temperature of 300° . The gases evolved were pumped out and the system tested for several days for leaks. The temperature was then slowly raised to 700° any gases evolved being pumped out. Enough specially purified hydrogen was then admitted to convert not over 90% of the calcium to hydride. After the calcium had had time enough to absorb 90 to 95% of the hydrogen (several days at this temperature), the gas remaining unabsorbed was quickly pumped out. All impurities which would not pass through the nickel were thus removed. The system was then held at a series of constant temperatures until a constant reading was obtained for the pressure of the hydrogen. Equilibrium pressures were approached from above and from below. To secure constancy of such pressures requires about a week at 800° . The securing of accurate results is, therefore, a very slow process.

A word of warning might not be out of place. The nickel cylinder works very well if not heated too high. At temperatures of 950-1000° the process of dissociation and diffusion takes place much more rapidly than at 800°, but the nickel cylinder undergoes a change, possibly forming an alloy with the calcium which then becomes nearly impermeable to hydrogen. No method was found of preventing this, and such cylinders were rendered useless.

Data

The results of three independent series of determinations are given in Table I. To obtain such data with the apparatus employed requires considerable time, several days being necessary to obtain a satisfactory equilibrium reading at the lower temperatures.

TABLE I
DISSOCIATION PRESSURES OF CALCIUM HYDRIDE AT DIFFERENT TEMPERATURES

Series 1 (Fig. 2 circle)			
T, °K.	P, cm.	1/T × 10 ³	Log ₁₀ P
1090	3.93	0.917	0.594
1126	7.75	.888	.889
1155	13.65	.866	1.135
1177	20.25	.850	1.306
1210	37.22	.826	1.571
Series 2 (Fig. 2 cross)			
1044	1.33	0.958	0.124
1065	2.04	.939	.310
991	0.42	1.009	-.377
1088	3.26	0.919	+ .513
1109	5.21	.902	.717
1131	8.01	.884	.904
1082	2.84	.924	.453
Series 3 (Fig. 2 ×)			
1011	0.45	0.989	-0.347
1041	1.13	.960	+ .053
1061	1.80	.942	.255
1091	3.53	.916	.548
1116	6.28	.896	.799

The results of these three runs are plotted on Fig. 2. The three sets of data agree reasonably well, giving a single curve. The greatest discrepancy occurs at the lowest temperature, where the pressures are lowest and are subject to the greatest error. In Fig. 3 we plot the results of several investigators in the field for comparison.

Discussion of Results

We are able to calculate the heat of reaction, ΔH , for the dissociation of calcium hydride from the relation

$$\frac{d \ln K_p}{d 1/T} = -\frac{\Delta H}{R}$$

where the symbols have their ordinary meaning and where $K_p = P_H$. We find from the slope of the curve, Fig. 2

$$\Delta H_{1100^\circ} = 51,100 \text{ calories}$$

If we use the equation

$$\Delta H = \Delta H_0 + 1.0 T$$

we are able to estimate $\Delta H_0 = 50,000$ calories.

Values for the heat of reaction have been given by several investigators. Guntz and Bassett give 46,200 calories as the heat of formation of solid

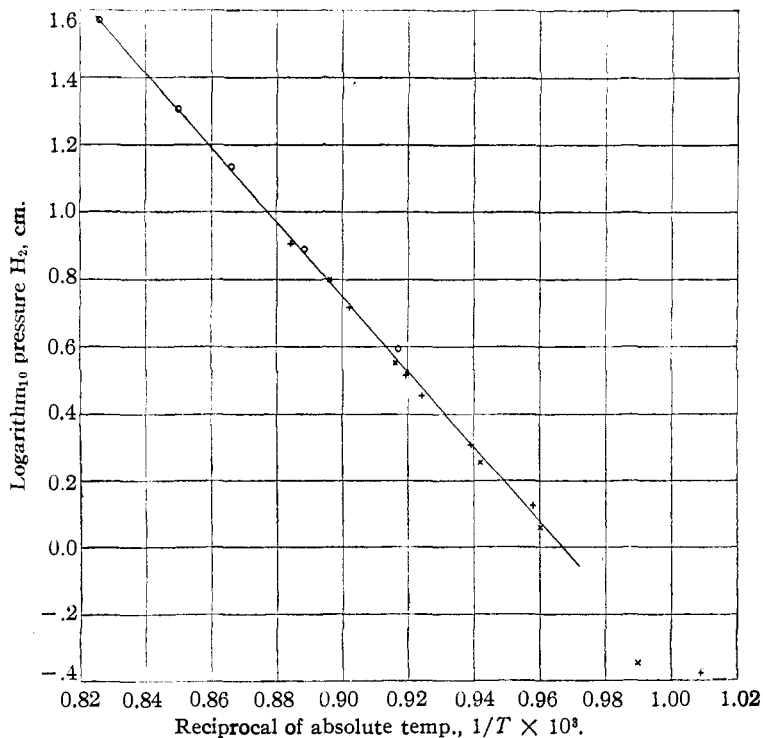


Fig. 2.

calcium hydride from its elements, calorimetrically determined, at ordinary temperatures. Brönsted gives a value of 45,100 while Kraus and Hurd with open cylinders found 48,400. Kassner and Stempel give 43,300 as the sum of the heats of reaction for their two stages. The data of Remy-Cenneté as shown by Fig. 3 would give about 50,000.

The value which we find for the heat of reaction, 51,100 calories, is seen to be considerably higher than former results, with the exception of the work of Remy-Cenneté. The agreement between our value and that of Remy-Cenneté is the more interesting, inasmuch as these two investigations utilize similar methods of confining the materials other than hydrogen which are present in the equilibrium mixtures.

The Mechanism of the Reaction

The opinions of various investigators in this field upon the course of the reaction for the dissociation of calcium hydride differ. All agree, apparently, that molecular hydrogen constitutes the gaseous product. The

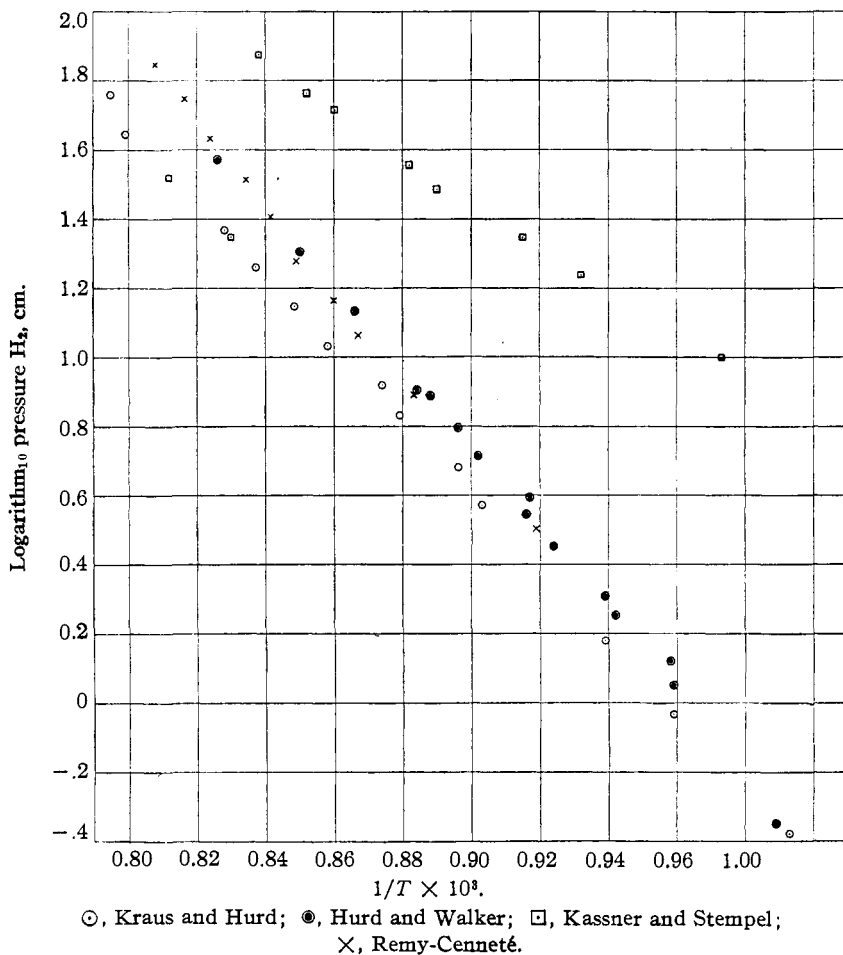
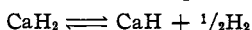


Fig. 3.—Comparison of results of several investigators on dissociation of calcium hydride.

composition of the solid product or products is not definitely determined, as we have already mentioned in this paper. The results of Kassner and Stempel for what they believe to be the equilibrium



are plotted in Fig. 3.

We have been unable to detect any such equilibrium in our investigation.

We have admitted 90% of the hydrogen necessary to react with a weighed quantity of calcium to form CaH_2 , and measured the equilibrium pressure at about 850° . Then at constant temperature we have withdrawn hydrogen by means of the pump in several steps until only about 20% of the hydrogen necessary to form CaH_2 was present. The equilibrium was allowed to establish itself after each withdrawal of hydrogen. The pressures measured agreed within the experimental error.

Experiments were also made where the equilibrium was approached by lowering the temperature from a higher temperature equilibrium. This, of course, caused an absorption of hydrogen and an increase of the combined hydrogen to calcium ratio. The same equilibrium pressure was found to establish itself as was found when the equilibrium was approached from a lower temperature, hydrogen having been removed.

We have not, in any case, added to the calcium more than 90% of the hydrogen, calculated as necessary to form CaH_2 with the weighed sample of calcium present in the nickel tube. Experiments are planned in which the calcium hydride will be formed by enclosing the calcium in the same type of closed nickel cylinder, placing this in a quartz tube, heating to 800° and passing a stream of pure hydrogen over it until the material has absorbed all the hydrogen possible. The tube will then be cooled to room temperature, still in hydrogen, removed, and placed in equilibrium apparatus shown in Fig. 1.

There is no apparent change in curvature of the $\log p$ against $1/T$ curve of Fig. 2 at the melting point of calcium, 810° , where $1/T \times 10^3 = 0.923$. Either these data are not sufficiently accurate to show this change of curvature or there is no calcium present.

Investigators who have worked with open containers have shown that calcium, if present, would have escaped from the containers at the higher temperatures, because of its appreciable vapor pressure. In the present investigation, only hydrogen could escape through the nickel cylinder, and we can, therefore, conclude nothing concerning the presence or absence of calcium.

Summary

An improved method for studying the thermal dissociation of calcium hydride has been described. The calcium hydride is contained in a closed nickel cylinder. This prevents action of the calcium or calcium hydride, on the quartz tube and removes a previous source of error in the determinations.

The method is recommended for any study where hydrogen is the only volatile constituent and where alloying does not occur with the nickel.

Three sets of data giving the equilibrium pressure of hydrogen as a function of temperature are given.

A graph, showing a comparison of results with those of other investigators, is given.

The value of the heat of reaction for the dissociation of calcium hydride is found to be 51,100 calories at 1100°K.

A brief discussion is given of the mechanism of the reaction.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE OXIDATION OF FREE ALKYL GROUPS. PHOTO- OXIDATION OF GASEOUS METHYL IODIDE

BY JOHN REGINALD BATES AND ROBERT SPENCE

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One of the greatest difficulties facing most investigations connected with the oxidation of gaseous organic compounds such as the hydrocarbons, is the occurrence, at the relatively high temperatures which have previously been necessary, of numerous incomplete side reactions. These side reactions mask the fundamental processes, making complete elucidation of reaction mechanisms from kinetic studies almost impossible. However, it can be shown that the photochemical oxidation of alkyl halides, occurring at 0°, is essentially the oxidation of free alkyl groups and an investigation of the photo-oxidation of methyl iodide, the simplest member of the series, seemed to promise some information regarding the fundamental processes of hydrocarbon oxidation.

Previous workers studying the action of light on alkyl halides dealt with the liquids, and have, for the most part, come to conflicting conclusions. Donnan and Burke¹ and Stobbe and Schmidt² found that oxygen was necessary for decomposition of ethyl iodide as determined by the production of iodine. Job and Empschwiler³ found that oxygen was not necessary for the decomposition of either ethyl or methyl iodides. In the former case they were able to obtain what was believed to be a photochemical "threshold" of reaction at 4100 Å., which was ascribed to the fact that the energy of this wave length coincided with the then accepted value for the C-I linkage. More recently, Iredale⁴ has determined the quantum yield of ethyl iodide decomposition in the absence of oxygen. This he finds to be unity, as measured by the iodine liberated, and therefore concludes that the primary process is the separation of an ethyl group and an iodine atom. Work on gaseous methyl iodide has been confined to its absorption spectrum, first studied by Herzberg and Scheibe.⁵ The absorption is con-

¹ Donnan and Burke, *J. Chem. Soc.*, **85**, 574 (1904).

² Stobbe and Schmidt, *Z. Wiss. Phot.*, **20**, 57 (1920).

³ Job and Empschwiler, *Compt. rend.*, **179**, 52 (1924).

⁴ Iredale, *J. Phys. Chem.*, **33**, 290 (1929).

⁵ Herzberg and Scheibe, *Trans. Faraday Soc.*, **25**, 716 (1928); *Z. physik. Chem.*, [B] **7**, 390 (1930).